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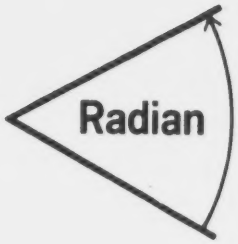

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FINAL REPORT
VOLUME I

OAP Contract No. EHSD 71-5

A THEORETICAL STUDY OF NO_x ABSORPTION USING AQUEOUS ALKALINE AND DRY SORBENTS

Presented to:

OFFICE OF AIR PROGRAMS
ENVIRONMENTAL PROTECTION AGENCY
411 West Chapel Hill Street
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This study was carried out to develop a theoretical description of aqueous scrubbing processes for NO_x emission control. The theoretical description is necessary to provide a basis for process development. The important chemical species present and the reactions they undergo in the sorption process were defined. An equilibrium model was developed so that the concentrations of the significant nitrogen-oxygen species present in the gas phase could be calculated under given conditions. A sorption mechanism and rate limiting step were proposed and an experimental program for testing them and providing engineering data was defined. Potential metal oxide sorbents were evaluated for effectiveness and efficiency on the basis of the thermodynamics of the sorption reactions.

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ABSTRACT

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1.0 INTRODUCTION

Nitrogen oxide emissions from stationary sources have been identified as the potential source of over half the NO_x emissions projected for the next thirty years. A recently published survey (BA-003) estimated that over three and one-half million tons of NO_x calculated as NO_2 were emitted by electric utilities alone in one year. The Environmental Protection Agency (EPA) has funded investigations into methods of reducing NO_x emissions in flue gases such as those produced by electric utilities. Only a few methods, namely combustion modification and flue gas treatment including aqueous scrubbing and selective reduction, were found to offer potential for NO_x control. Further, none of the suggested flue gas treatment processes have been applied to NO_x control for electric utility flue gases. The methods are still in the early stages of process development.

This report presents the results of an effort to theoretically describe a process for reducing NO_x emissions in flue gases such as those produced by electric utilities. The process under investigation was flue gas treatment by aqueous scrubbing. The goal of this work was to develop a theoretical description of the aqueous scrubbing process. A theoretical description was a necessary prerequisite for successful process development because the basic chemical and chemical engineering aspects of the process had not been previously described. Four steps needed to make a theoretical description to aid in process development will now be given.

1. Literature Survey and Problem Definition

These tasks are described in Sections 2.0 and 3.0 of the report. They involved becoming familiar with what had already been published concerning aqueous scrubbing for flue gas treatment. In addition, they involved defining the scope of the problem by specifying what important chemical species and reactions take place in the process and what the rate controlling steps might be. The problem definition revealed that flue gas composition and the concentration of the many different nitrogen species present determined some very basic aspects of the process. Specifically they gave a strong indication of what the rate controlling step and the sorption mechanism might be. This fact pointed the way for the second step in developing a theoretical description.

2. Development of the Composition-Concentration Model

The second step in providing a theoretical description of the aqueous scrubbing process was to develop a model by which the concentrations of the various nitrogen-oxygen compounds present in aqueous scrubbing systems could be calculated. This model is described in Section 4.0 of the report.

3. Cooperation with EPA In-House Experimental Program

A third phase of the program involved experimentally testing the concepts proposed in the theoretical description. An in-house experimental program to study NO_x sorption in packed towers was in progress during the period of performance of this study. While the hypotheses developed from the theoretical description were not completely tested during the rough screening studies carried out by EPA, some valuable information as well as considerable practical experience were gained. These studies are discussed in Sections 5.0 and 6.0 of the report.

4. Screening of Candidate Metal Oxide (Hydroxide) Sorbents

One of the main goals of the program was to use the theoretical description to predict which metal oxides (hydroxides) would be the most effective and efficient sorbents in an aqueous or a dry scrubbing process. The screening of candidate sorbents was done on the basis of the thermodynamics of their reactions with nitrogen oxides. This task is discussed in Section 7.0 of the report. The results are limited to processes in which a solid nitrate is formed in the sorption step and decomposed in the regeneration step.

Throughout the course of this study there were numerous cases in which it was necessary to know the thermodynamic properties of the nitrogen oxides, oxyacids, the metal oxide (hydroxide) sorbents and the sorption products. In addition, values for equilibrium constants for decomposition, dissociation, ionization,

vaporization and sorption reactions were needed. Finally, activity coefficients for aqueous phase species were necessary. These thermodynamic data were obtained from the literature using careful evaluation and in some cases, recalculation. Some of the properties for solids were estimated. The acquisition and use of thermodynamic properties are discussed in Section 8.0 of the report. Section 9.0 gives a summary of the results of the program. The references cited in Volume I are given in Section 10.0. Volume II contains the actual details of most of the work. As work packages were completed during the study, they were documented in detail in technical notes. The technical notes which are referred to quite frequently in Volume I are contained in Volume II. Volume II also contains a listing of the computer program written to perform the composition-concentration model calculations.

2.0 LITERATURE SURVEY

The first task in the investigation of aqueous alkaline scrubbing was to collect existing published data and become familiar with what had already been reported concerning the problem. This section describes the type of information that was sought, the sources that were used to collect information and the general types of information that were found.

2.1 Information Sought

The goal of the program was to describe the thermodynamics of regenerative aqueous alkaline processes for removing NO and NO_2 from gas mixtures. This was to be the thermodynamic basis for screening and selecting potential metal hydroxide sorbents. A further goal of the program was to determine the sorption mechanism and develop a description of the chemical engineering unit operations involved. This was to be done in conjunction with EPA inhouse experiments.

The accomplishment of these goals required the kinds of information described below.

- Reactions between nitrogen oxides and aqueous solutions: equilibrium constants, kinetic data, mechanisms.

- Physical, chemical and thermodynamic properties of gaseous, aqueous and solid nitrogen oxides and oxyacids, metal nitrates, nitrites, hydroxides, and carbonates: standard state thermodynamic properties, vapor pressures, solubilities, activity coefficients, thermal stabilities.

Descriptions of existing processes for aqueous sorption of NO and/or NO_2 from gaseous mixtures.

2.2 Sources of Information

Three sources for acquisition of pertinent literature were used. The source from which most of the references of interest were obtained was Chemical Abstracts. Cumulative subject indices covering references published from 1947 to 1966, as well as semiannual subject indices for the period 1967 to June, 1969, were searched. The biweekly issues from July, 1969, to October, 1970, were searched using the key word index at the end of each issue. Slightly less than 1000 abstracts were selected.

A second useful information source was publications from EPA's Air Pollution Technical Information Center. Air Pollution Abstracts and Nitrogen Oxides: An Annotated Bibliography were both consulted. In addition, Tom Kittleman of EPA provided the computer listing of abstracts from an APTIC search on nitrogen oxides and absorption.

A third source of information was the final report "Systems Study of Nitrogen Oxide Control Methods for Stationary Sources" prepared for EPA under contract PH 22-68-55. Section 5.5.1 dealt with aqueous absorption of NO_x and the bibliography for that section gave several pertinent references. In addition, the supplementary bibliography of 750 references was searched and some additional titles were selected as potentially interesting. Many of these were duplications of references already found using APTIC publications.

2.3 Information Found

The abstracts and titles collected during the literature search were reread and filed in categories with descriptive titles. These files were consulted at appropriate later times when new phases of work were begun. Much of the literature is reviewed in technical notes. Some of the references collected were not found to be useful at any time during the period of contract performance, but they are potentially useful for future work. Some of the references served to point out what isn't known rather than what is known. Finally, the numerous abstracts collected concerning descriptions of and operating data for aqueous scrubbing processes were particularly useless for this work.

The details of what types of information were found are discussed in Technical Note 200-007-14 in Volume II of this report. The note contains a supplemental bibliography which lists most of the references found during the literature search in categories with descriptive titles. It should be kept in mind that the categories are only broadly descriptive, and some references could undoubtedly be filed in more than one category. The filing of references in each category was done by reading the abstract, since the titles alone are not always indicative of the content.

3.0 PROBLEM DEFINITION

The goal of this program was to conduct a theoretical study of aqueous alkaline sorption processes involving metal oxide (hydroxide) sorbents and use the theoretical framework to help answer the following:

- What is the sorption mechanism (to be done in conjunction with EPA experiments)?
- What metal oxide (hydroxide) sorbents are capable of or most effective for removing NO_x from flue gases?

3.1 Scope of the Problem

The most important goal was to develop a theoretical description of sorption of NO_x in the scrubber. This description, combined with experimental data, would indicate the technical feasibility of aqueous sorption processes. In view of the EPA experimental results, it appeared that the most important question was whether or not the nitrogen oxides could be removed in the scrubbing step. However, it is realistic to consider also what will be done with the scrubbing liquor after it contains the nitrogen oxides which have been removed from the flue gas. Regenerative processes were to be considered. After all, converting an air pollution problem into a water pollution problem is not a practical solution. Therefore, the goal was to derive a theoretical description not only for the scrubber but for an entire process.

A flue gas composition was assumed for computational purposes in the thermodynamic screening studies. The composition is given in Table 3-1.

TABLE 3-1
COMPOSITION OF GAS MIXTURE FROM WHICH NITROGEN OXIDES MUST BE REMOVED

Component	Approximate Concentration (mole%)
N_2	76
CO_2	13
H_2O	7
O_2	3
NO_x	0.05 (500 ppm)

Gas mixtures having the composition shown in Table 3-1 are typical of those emitted by natural gas burning power plants or oil or coal burning plants whose off gases have been treated for SO_2 removal (LO-007). Vapor phase and aqueous phase interaction of nitrogen oxides and sulfur oxides is quite complicated. The number of possible reactions which can take place imposes an almost insurmountable problem for the development of a theoretical description. Therefore, it is logical and useful to develop a theoretical description for the already complicated system described in Table 3-1 before the description of an even more complicated system is attempted.

The composition of the gas mixture described in Table 3-1 has important implications for the study of aqueous alkaline scrubbing. The nitrogen oxides make up only 0.05 mole% (500 ppm) of a typical flue gas, while 13 mole% CO_2 is present. An alkaline sorbent will remove CO_2 as well as nitrogen oxides

especially since the CO_2 is present in much greater concentration. The Radian aqueous phase equilibrium model (LO-007) was used to calculate the results of sorption of a gas containing 10% CO_2 into scrubber solutions composed of .05 molar and 1.0 molar NaOH. The calculated values of pH and ionic strength at 40, 50, and 60°C are shown in Table 3-2.

TABLE 3-2
SOLUTIONS IN EQUILIBRIUM WITH A GAS
GAS CONTAINING 0.10 atm CO_2

	pH at Equilibrium	
T (°C)	Initial Conc. NaOH = .05 M	Initial Conc. NaOH = 1.0 M
40	7.53	8.51
50	7.61	8.56
60	7.71	8.62
	(I = .05)	(I = .84)

The calculated results shown in Table 3-2 have been confirmed experimentally. Streight (ST-012) reported absorbing a synthetic waste gas containing .05% NO_2 and 2.4% CO_2 using "dilute caustic" of pH 12.8 in a 12-inch i.d. column with five feet of packing. The CO_2 converted the sorbent to sodium carbonate and the pH decreased to a little above seven. The implication is that it is impossible to carry out alkaline (OH^-) scrubbing on flue gas containing 13% CO_2. The CO_2 will be removed by an alkaline solution until equilibrium is reached and the pH is lowered to a value in the range of seven to nine. Nitrogen oxides will then continue to be absorbed, liberating CO_2.

3.2 Theoretical Framework

A theoretical description of the processes considered had to be developed as a basis for predicting which sorbents would be effective in removing NO and NO_2. In order to be useful for engineering predictions, the theoretical framework had to include the following.

- What chemical species are present and in what reactions are they involved during sorption and regeneration?
- What is the rate limiting step in the sorption process and what species are involved in the rate limiting step?
- What are the free energy changes involved in the processes and which sorbent has the most efficient free energy change. An efficient free energy change is one that is large enough to supply sufficient driving force for the process but not so large that a large free energy reversal will be required in the regeneration step.

The theoretical framework was then developed in the following way. The possible species present and the reactions they can undergo were listed and studied to discern what takes place in the system. Next, all the diffusion, reaction, and mass transfer steps involved in going from $NO_{x(g)}$ to $NO_{2(\ell)}^-$ and $NO_{3(\ell)}^-$ were studied and the rate controlling step was proposed. Then the problem was formulated in terms of the species significant for the mass balance and in terms of the species involved in the rate controlling step. As will be seen from the following

discussion the problem of describing the path from $NO_{x(g)}$ to $NO_{2(\ell)}^-$ and $NO_{3(\ell)}^-$ is very complicated. First the possible species and reactions are described. Then the rate controlling step is discussed.

3.2.1 Species and Reactions

The nitrogen oxides to be removed from the flue gas are NO, nitric oxide, and NO_2, nitrogen dioxide. The sum of their concentrations is usually referred to as NO_x. Even though the 500 ppm NO_x typically present in flue gases is 90% nitric oxide, NO_x concentrations are usually reported as equivalent NO_2. There are several reasons for the preference for NO_2. First, many of the analytical methods used involve oxidation of nitric oxide to NO_2 and measurement of total NO_2 concentration. Nitrogen dioxide is easily measured spectrophotometrically; it is a brown colored gas. Also, NO_2 is more reactive than NO and can be absorbed more easily by more solvents. Most research has centered on studying the absorption of NO_2 rather than NO.

The concentration of NO_x as equivalent NO_2 is a useless description of the nitrogen oxides in the vapor phase if one is concerned with the development of a theoretical framework. The species listed in Table 3-3 all exist in some concentration in the gas phase. The subscript (g) has been eliminated, so that NO, for example, is understood to be $NO_{(g)}$.

TABLE 3-3
GAS PHASE SPECIES IN THE NO_x-H_2O SYSTEM

NO	N_2O
NO_2	N_2O_5
N_2O_3	H_2O
N_2O_4	HNO_2
O_2	HNO_3
N_2	

The species listed in Table 3-3 are present in widely varying concentrations. They interact with each other in many possible reactions. Which of these species and reactions should be used to describe the gas phase for the sorption process is a question of basic importance. Some species and reactions can be eliminated from consideration in the theoretical description. For instance, some species are present in relative concentrations that cause them to be unimportant for mass balance. These species can be disregarded in the problem formulation, but only if they are not involved in a process or step that is rate limiting. On the other hand, some species that are present only in small concentrations and are not involved in rate limiting steps are still included in the problem formulation for convenience. An example is N_2O_5, which is a convenient species to consider in nitrate thermal decomposition calculations. Stern (ST-026) reported that the decompositions of NO and NO_2 to form the elements need not be considered since the reactions are very slow at temperatures below 1000°K. Reactions involving N_2O are also slow. Based on the reasons just discussed, the reactions in Equations 3-1 through 3-6 were used to describe interactions in the gas phase.

$$NO + NO_2 \rightleftarrows N_2O_3 \qquad 3\text{-}1$$

$$2NO_2 \rightleftarrows N_2O_4 \qquad 3\text{-}2$$

$$N_2O_3 + H_2O \rightleftarrows 2HNO_2 \qquad 3\text{-}3$$

$$N_2O_4 + H_2O \rightleftarrows HNO_2 + HNO_3 \qquad 3\text{-}4$$

$$NO_2 + N_2O_4 \rightleftarrows NO + N_2O_5 \qquad 3\text{-}5$$

$$NO + \tfrac{1}{2}O_2 \rightleftarrows NO_2 \qquad 3\text{-}6$$

Reactions 3-1, 3-2 and 3-3 have been reported to be rapid enough to be considered at equilibrium for the purposes of this study (CH-032, p. 55; WA-014; WA-015, pp. 11-12; WA-016). There is some disagreement concerning whether or not reaction 3-4 is a homogeneous reaction and whether or not it can be considered to be at equilibrium. Reaction 3-6 is a slower reaction; it is the rate limiting step for nitric acid production (CH-032). It cannot be considered to be at equilibrium for purposes of describing mass transfer in a scrubber where the residence time would be on the order of seconds. It could be considered to have reached equilibrium in a static nitrate thermal decomposition experiment where the product gases are not removed and the duration of the decomposition is on the order of several minutes to an hour. Reaction 3-5 is included for convenience in the screening process.

The number of possible species in existence in the aqueous phase is even greater than the number in the gas phase. In addition, the set of possible reactions is much more complicated and the equilibria are not completely described in the literature. Waldorf (WA-015) discussed the problem at length in his dissertation, "Reactions and Equilibria in the Nitrogen Oxides-Water System", which included a comprehensive literature review. The species listed in Table 3-4 can exist in the aqueous phase. These were identified from a review of the chemistry of the system $NO\text{-}NO_2\text{-}H_2O$. The subscript (ℓ) has been eliminated for convenience so that NO, for example, is understood to be $NO_{(\ell)}$.

TABLE 3-4

AQUEOUS PHASE SPECIES IN THE $NO_x\text{-}H_2O$ SYSTEM

NO	HNO_3	NO^+
NO_2	H^+	NO_2^+
N_2O_3	OH^-	$HONOH^+$
N_2O_4	NO_2^-	$HONONO^+$
HNO_2	NO_3^-	$HNO_3 \cdot H_2O$
H_2O		NO_2NO^+

It has been proposed by numerous authors including Moll (MO-008) and Gray and Yoffe (GR-004) that the dimers N_2O_3 and N_2O_4 either ionize or form ion pairs according to the following scheme.

$$N_2O_4 \rightleftarrows NO_2^+NO_2^- \rightleftarrows NO^+NO_3^- \qquad (3\text{-}7)$$

$$N_2O_3 \rightleftarrows NO^+NO_2^- \qquad (3\text{-}8)$$

The species $HONOH^+$ (BU-009), $HONONO^+$ (WA-006) and NO_2NO^+ (MI-004) have had tentative spectroscopic identification. Some of the species listed in Table 3-4 exist only under extreme conditions of pH which probably will not be encountered in the processes studied. These can therefore be eliminated from our formulation. They may become of importance later if processes other than aqueous alkaline scrubbing are investigated. Additional species can be eliminated from the aqueous phase formulation with no difficulty if their relative concentrations cause them to be unimportant in the mass balance and they are not involved in a rate limiting step.

The aqueous phase reactions which involve ionic species are considered to be quite rapid. If an aqueous phase reaction is the rate controlling step for sorption of NO and NO_2, it will be necessary to know the mechanism of the reaction, i.e., the individual, serial, usually bimolecular steps which occur and which result in the overall stoichiometry. The mechanism according to which nitrogen oxides react with water to form nitrous and nitric acids is not known. Several possibilities have been discussed in the literature. The overall stoichiometries are given in (3-9) and (3-10).

$$NO + NO_2 + H_2O \rightleftarrows 2HNO_2 \rightleftarrows 2H^+ + 2NO_2^- \quad (3\text{-}9)$$

$$2NO_2 + H_2O \rightleftarrows HNO_2 + HNO_3 \rightleftarrows 2H^+ + NO_2^- + NO_3^- \quad (3\text{-}10)$$

Some proposed mechanisms are given in (3-11) through (3-13).

$$N_2O_4 \rightleftarrows \begin{matrix} NO^+NO_3^- \\ \text{or} \\ NO^+ + NO_3^- \end{matrix} \xrightarrow{H_2O} HONOH^+ + NO_3^- \rightarrow 2H^+ + NO_2^- + NO_3^- \quad (3\text{-}11)$$

$$N_2O_3 \rightleftarrows \begin{matrix} NO^+NO_2^- \\ \text{or} \\ NO^+ + NO_2^- \end{matrix} \xrightarrow{H_2O} HONOH^+ + NO_2^- \rightarrow 2H^+ + 2NO_2^- \quad (3\text{-}12)$$

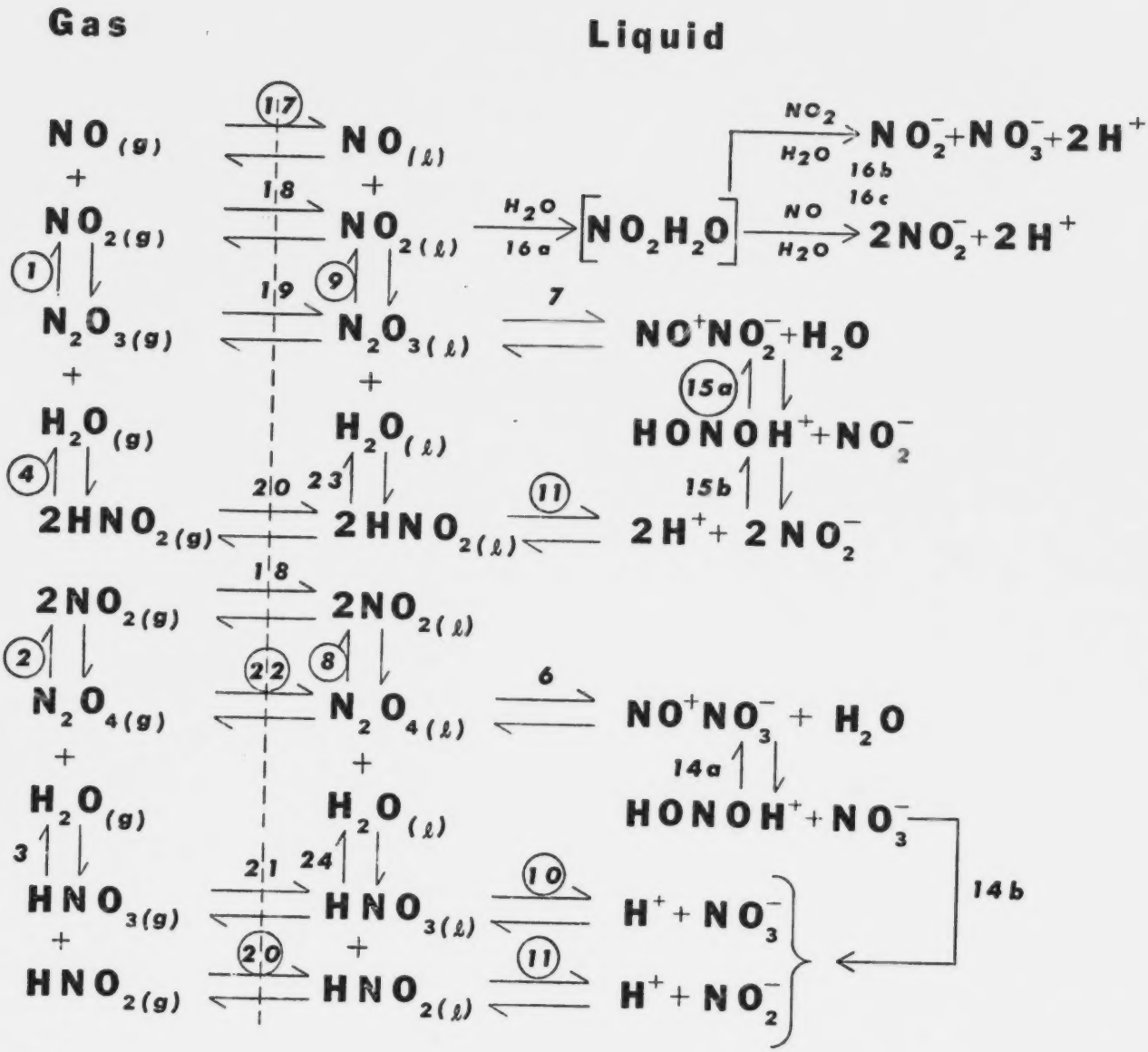
$$NO_2 + H_2O \longrightarrow x \quad (3\text{-}13a)$$

$$x + NO_2 \xrightarrow{H_2O} NO_3^- + NO_2^- + 2H^+ \quad (3\text{-}13b)$$

$$x + NO \xrightarrow{H_2O} 2NO_2^- + 2H^+ \quad (3\text{-}13c)$$

The mechanism for the nitrogen oxides-water reaction in the aqueous phase will not have to be known unless the reaction is rate controlling for the sorption process.

A summary of the possible species and reactions in the gas and aqueous phase systems containing nitrogen oxides and water is shown in Figure 3-1. The reactions or mass transfer steps which have been studied experimentally and for which equilibrium constants have been reported in the literature are indicated in the figure by those numbers which are circled.


Gas
Liquid
NO(g) + NO2(g)
N2O3(g) + H2O(g)
2HNO2(g)
2NO2(g)
N2O4(g) + H2O(g)
3 HNO3(g) + HNO2(g)
NO(ℓ) + NO2(ℓ)
N2O3(ℓ) + H2O(ℓ)
2HNO2(ℓ)
N2O4(ℓ) + H2O(ℓ)
HNO3(ℓ) + HNO2(ℓ)
NO2H2O
NO+NO2− + H2O
HONOH+ + NO2−
2H+ + 2NO2−
NO+NO3− + H2O
HONOH+ + NO3−
H+ + NO3−
H+ + NO2−
NO2 / H2O → NO2− + NO3− + 2H+
H2O → NO2H2O → NO / H2O → 2NO2− + 2H+
1 2 3 4 5 6 7 8 9 10 11 14a 14b 15a 15b 16a 16b 16c 17 18 19 20 21 22 23 24

◯ Reactions for which equilibrium or dissociation constants have been measured

FIGURE 3-1

Species and Reactions in the Gas and Aqueous Phase System NO_x-H_2O.

3.2.2 Rate Controlling Step

Figure 3-1 shows the various paths by which the gaseous nitrogen species can be transformed into aqueous nitrogen containing ions or neutral aqueous species. The process involves chemical reaction and molecular diffusion in the bulk gas up to the gas-liquid interface, gas film diffusion, liquid film diffusion, and then diffusion and chemical reaction in the aqueous phase. All of these steps are seen as resistances to mass transfer and one step will probably be the rate controlling step. The problem discussed in this section is how to describe the rate of sorption. One of the paths shown in Figure 3-1 will be the fastest path. The slowest step in this fastest path will be the rate controlling step. Rate equations must be written in order to size equipment for a sorption process. The rate equation must describe the rate of removal of gaseous nitrogen oxides in the scrubber in terms of the change in concentration of one of the species in Figure 3-1. It is best to use either the concentration of the species involved in the rate controlling step or the concentration of the species with which it is in equilibrium.

3.2.2.1 Mechanism Suggested in the Literature

Numerous studies have been conducted to investigate the rate of nitrogen oxides sorption by aqueous solutions in varying types of equipment. Other studies have been carried out to determine simply the rate of reaction between nitrogen oxides and water. The experimental results of the various investigators and the mechanisms and rate determining steps they proposed were studied in detail and are reviewed in Technical Note 200-007-02 entitled "Review of the Literature on Experimental Studies of the

Aqueous Absorption of Nitrogen Oxides". The note is included in Volume II of this report. The results were obtained for widely varying experimental conditions using acidic neutral and alkaline sorbents for gas mixtures containing NO alone, NO_2 alone, and mixtures of the two. With the exception of one or two studies, the lowest concentration of nitrogen oxides studied was 0.5 mole%, which is a whole order of magnitude greater than the concentration range for flue gases. Few of the investigators made material balances or even measured anything except $NO_2(g)$. Many of the results appear to be contradictory. Since the experimental conditions were so diverse, it was difficult in the beginning to make generalizations about the results or to apply them to the problem at hand. To facilitate comparisons, each of the results was summarized consistently in a table with separate columns describing gas composition, absorbing medium, apparatus and operating conditions, quantities measured, and results and discussion.

The data concerning sorption of pure nitric oxide or pure nitrogen dioxide or those gases diluted only with nitrogen will not be discussed in detail here. They are summarized in the technical note. Nitric oxide sorption with no NO_2 present has been investigated to a limited extent by workers in the field of coke oven gas purification. Nitric oxide impurities of even a few ppm must be removed from coke oven gas to prevent their reaction with dienes to form explosive resins. Nitrogen dioxide sorption with no NO present has been studied widely because of nitric acid manufacture where relatively high concentrations of NO_2 are absorbed by dilute nitric acid solutions. Much early effort was devoted to showing that the rate of NO_2 sorption is proportional to the concentration of N_2O_4 and that the rate of the N_2O_4 reaction with water might be rate controlling for NO_2 sorption. Not until fairly recently have investigators

considered how the presence of nitric oxide might affect the rate of NO_2 sorption. These investigations were still carried out in the interest of nitric acid manufacture, and virtually no one has investigated nitrogen oxides sorption in the context of flue gas purification.

Investigations concerning the rate of sorption and the rate limiting step for sorption from gas mixtures containing both NO and NO_2 were studied in detail. None of the investigators actually answered the questions of what is the rate limiting step and what species should be used in the rate equations for the particular case of interest, i.e., flue gas cleaning. It is tempting, nevertheless, to select the most reasonable mechanism and the resulting rate equations, and to apply them to the problem. While it would save a lot of hard thinking, the results would not be useful. The following paragraphs give a general description of what was found in the literature. Then the research that has a bearing on the problem of flue gas NO_x removal is discussed in more detail. The contributions are subtle since only points of view and ideas from the literature were used rather than detailed mechanisms or actual rate equations.

Twenty two of the publications reviewed concerning the rate of nitrogen oxides sorption dealt with absorption from gases initially containing both nitric oxide and nitrogen dioxide. The initial total concentrations varied from about 0.5 to 100%. Absorbents studied were water and aqueous solutions of HNO_3, NaOH, $CaCl_2$, Na_2CO_3, $Ca(NO_3)_2$, $Ca(OH)_2$, $CaCO_3$, Na_2CO_3 + NaOH + $NaHCO_3$, and Na_2CO_3 + $NaNO_2$ + $NaNO_3$. A variety of equipment was used including wetted wall columns, packed columns, venturi scrubbers, spray columns, laminar jet apparatus, sieve plate absorbers, and a horizontal mechanical absorber with a rapidly revolving axial shaft.

There was some agreement (VA-009, VA-006, MI-005) that the absorption rate from NO-NO_2 mixtures in one particular concentration range is a maximum at a 1:1 mole ratio of NO_2 to NO or at 50% oxidation. These results are well expressed graphically by Hofmeister and Kohlhaas (HO-009). Some agreed that the absorption rate is proportional to the concentration of N_2O_3 or to the product of NO and NO_2 concentrations (KR-007, ZH-001, EL-004, KO-026). Perelman (PE-010) and Zhavoronkov (ZH-002) and several other workers have stated that the rate of N_2O_3 absorption is greater than the rate of N_2O_4 absorption. Atroshchenko (AT-005) found that the relative rates depend on the experimental apparatus. Ganz (GA-009, GA-010) found the rates to be about equal in his apparatus. Koval (KO-024, KO-026) reported the rate of reaction of N_2O_3 with water to exceed the rate of reaction of N_2O_4 with water. Kramers, et al. (KR-006) and Hofmeister and Kohlhaas (HO-009) measured the rates of the individual reactions using a laminar jet apparatus and the penetration theory.

There was wide agreement (GA-014, PE-010, KR-007, MU-004, GA-008, KR-008) that the concentration of nitrate and nitrite ions in the sorbent has an effect on the rate of sorption. All reported that an increase in nitrate and nitrite concentration reduces the rate of sorption. Perelman (PE-010) reported the rate to increase for sorbents in the order $CaCO_3$, Na_2CO_3, $Ca(OH)_2$. Atroshchenko (AT-005) and Caudle and Denbigh (CA-014) reported the sorption rate was greater in water than in HNO_3 or $CaCl_2$ solutions, respectively. There was agreement among several workers (KR-008, VA-006, PO-015) that, above a lower limiting value, the concentration of Na_2CO_3 in the sorbent had no effect on the sorption rate.

The work of several authors merits more detailed discussion. Of particular interest for the problem at hand is the work of Andrew and Hanson (AN-001) who stated that the mechanism and thus the rate of absorption is dependent on the relative and total concentrations of NO and NO_2. Most important, they showed that to explain the rate of NO_x sorption over a wide range of gas concentrations, it is necessary to use more than one mechanism. They described four possible absorption mechanisms and developed theoretical rate equations for a laboratory sieve plate for each mechanism. The rate equations were expressed in terms of the plate efficiency, η, defined as:

$$\frac{\text{Chemical } NO_2 \text{ Absorbed}}{\text{Chemical } NO_2 \text{ Entering}}$$

Chemical NO_2 was defined by Andrew and Hanson as $NO_2 + 2N_2O_4 + N_2O_3 + \frac{1}{2}HNO_2$. A discussion of the mass balance equations for NO and NO_2 is given on pages 34-35. They compared plate efficiencies predicted from the theoretical rate equations with actual measured plate efficiencies. Figure 3-2 shows the plate efficiencies predicted for each mechanism as a function of chemical NO_2 concentration for a fixed $NO:NO_2$ ratio of 1.0. Some physical constants had to be estimated to construct the figure. The mechanisms numbered one through four in Figure 3-2 are described in the legend below.

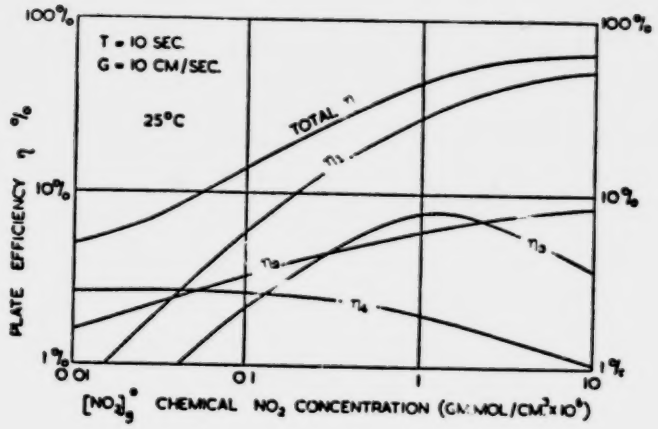


FIGURE 3-2 - PREDICTED PLATE EFFICIENCIES BASED ON THE THEORETICAL RATE EQUATIONS OF ANDREW AND HANSON [Taken from: Chem. Eng. Sci., 14, 105-13 (1961)]

η_1 Percent of total plate efficiency due to Mechanism 1: diffusion across gas and liquid films as NO_2 and N_2O_4; subsequent hydrolysis to HNO_2 and HNO_3; decomposition of HNO_2 to N_2O_3, $N_2O_3(g)$ or $HNO_2(g)$ given off. NO_2-N_2O_4 diffusion rate limiting.

η_2 Percent of total plate efficiency due to Mechanism 2: diffusion as $HNO_2(g)$-$N_2O_3(g)$ equilibrium mixture; HNO_2 decomposition in aqueous phase; nitric oxide given off. Aqueous HNO_2 decomposition and $NO_{(g)}$ diffusion rate limiting.

η_3 Percent of total plate efficiency due to Mechanism 3: gas phase formation of HNO_2 and HNO_3, $HNO_{3(g)}$ dissolution in water vapor forming mist, $HNO_{3(g)}$ diffusion into aqueous phase. Rate limited by gas phase HNO_3 formation.

η_4 Percent of total plate efficiency due to Mechanism 4: liquid film limited diffusion of NO_2, dimerization in solution and hydrolysis of N_2O_4. $HNO_{2(g)}$ given off.

Figure 3-3 shows the total plate efficiencies measured by Andrew and Hanson as a function of chemical NO_2 for two different relative concentrations of nitric oxide and nitrogen dioxide. The experimental data are indicated by O's and X's, while the predicted efficiencies are indicated by the solid lines.

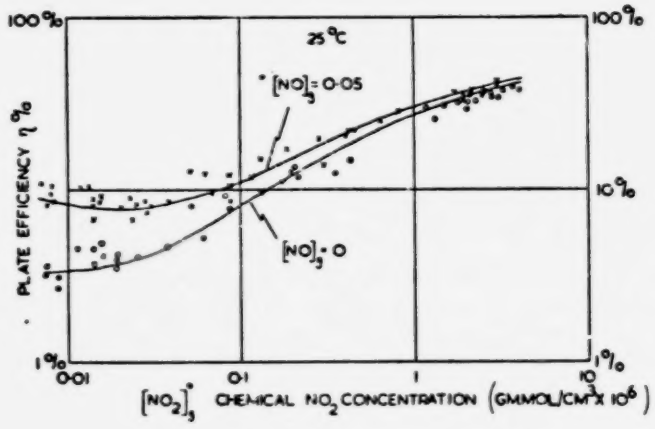


FIGURE 3-3 - COMPARISON OF ANDREW AND HANSON'S MEASURED AND PREDICTED TOTAL PLATE EFFICIENCIES
[Taken from: Chem. Eng. Sci., 14, 105-13 (1961)]

Using Figure 3-2 one could determine the mechanism which makes the greatest contribution to plate efficiency (absorption rate) for different chemical NO_2 concentrations at a fixed ratio of NO/NO_2. Since Andrew and Hanson were primarily interested in nitric acid manufacture, they only showed data for a fixed NO/NO_2 ratio and not for a variety of compositions. Their main concern was how a change in chemical NO_2 concentration was reflected in a change in rate determining step and mechanism. In addition, they used mass transfer coefficients determined for a laboratory sieve plate absorber and equilibrium constants which might or might not agree with the ones used by Radian. As a result, the rate equations and mechanisms are not directly applicable to the problem of flue gas sorption in a packed tower. A valuable result of their work, however, is the idea that the rate determining step and the sorption mechanism are peculiar to the gas composition and concentration. However reasonable and theoretically sound a mechanism appears, if it describes gas mixtures whose compositions and concentrations differ from those in flue gas, the mechanism may not be applicable to flue gas cleaning.

The work of Koval (KO-026) concerns the effect of adding nitric oxide on the absorption of $NO_2 + N_2O_4$ by water. Again the investigations were prompted by a desire to understand the mechanism of nitric acid manufacture. The work seems to have been performed with great care and the proposed mechanism did explain some results found by previous workers. Although Koval did not measure the rates predicted by the rate equations resulting from his mechanism, he did make material balances and demonstrate that the stoichiometry resulting from his mechanism agreed with the actual stoichiometry.

Koval pointed out indirectly one of the main problems in evaluating NO_x sorption systems and in NO_x sorption process design. The problem is that nitrogen exists in so many different oxidation states and ionic or molecular forms that it is very complicated to keep track of them all. Analytical chemistry techniques and calculation of material balances become a problem. Koval realized these problems because he was one of the few investigators to attempt to make a material balance. Even when sorption of pure NO_2-N_2O_4-nitrogen mixtures is studied, the concentration of HNO_2-N_2O_3-NO must be taken into account. Some investigators ignored their affect or treated their concentrations as negligible. In order to account for the different forms of nitrogen, analytical techniques had to be developed. Koval observed that many investigators mistakenly titrated acidic liquid absorption products directly with sodium hydroxide. He showed that decomposition of HNO_2 between the time of sampling and analysis could result in values for total acid from four to twenty percent too low. In addition the titration of nitrous acid with sodium hydroxide does not have a sharp end point since HNO_2 is always decomposing and the pH is not constant with time. Waldorf (WA-015) studied instrumental analytical techniques which provide one means of solving the analytical problems. He also pointed out the lack of reliable activity data and the fact that most investigators did not analyze the aqueous phase for anything other than nitrate ("nitric acid").

The mechanism and rate determining step for NO_x sorption also depend on the apparatus and the amount of gas-liquid contact area that can be provided. Koval (KO-026) demonstrated this by conducting experiments in a variety of equipment types with other factors held constant. Ganz and coworkers (GA-010, GA-013, GA-014) describe a high speed horizontal mechanical absorber with a revolving axial shaft which is said to provide an increase in sorption capability

over conventional gas-liquid contactors by increasing gas and liquid turbulence. They reported precipitation of basic nitrate salts beyond some critical concentrations of CaO, $Ca(NO_2)_2$ and $Ca(NO_3)_2$. Gorfunkel (GO-007) also reported the possibility of formation of $CaO \cdot Ca(NO_3)_2 \cdot 2H_2O$. The mechanism proposed by Ganz for the mechanical absorber includes the suggestion that "liquid phase" oxidation according to Equation 3-14 takes place.

$$NO_2^-(\ell) + NO_2(g) \rightleftarrows NO_3^-(\ell) + NO(g) \qquad (3\text{-}14)$$

The reaction was suggested to account for the greater than theoretical amounts of nitrate and less than theoretical amounts of nitrite produced in the mechanical absorber.

In summary, none of the mechanisms and rate controlling steps proposed in the literature for NO_x aqueous sorption were directly applicable to sorption of NO and NO_2 from power plant flue gases. Most of the research results are inapplicable because they deal with gas compositions and concentrations outside the range of those in flue gas. In particular, a great amount of work has been published concerning the problem of NO_2 sorption in nitric acid production. The concentration of nitric oxide in those systems does not exceed that of NO_2. However, several important ideas concerning the mechanism and rate determining step for aqueous sorption were gained from the literature published on NO_x sorption. First, the mechanism and rate determining step are dependent on the gas composition (ratio of NO/NO_2), the total nitrogen oxides concentration, and the type of gas-liquid contactor employed. The mechanism and rate equations proposed to date are not applicable to flue gas cleaning processes. Second, since the nitrogen oxides-water system is

complicated in both the aqueous and gaseous phases by the many stable oxidation states of nitrogen, material balances and analytical techniques are very important in establishing a mechanism.

3.2.2.2 Proposed Method for Determining Rate Controlling Step for Flue Gas Treatment Processes

Since no applicable work has been published concerning the rate controlling step, it was decided one should be proposed for flue gas treatment on the basis of gas composition and concentration and mass transfer characteristics for packed towers. Then the proposed mechanism had to be tested by conducting absorption experiments and measuring enough gas and liquid phase concentrations to be able to calculate material balances. One important tool was needed to describe mass transfer from a gas phase containing numerous nitrogen species at equilibrium to a liquid phase containing numerous nitrogen species at equilibrium. This was the ability to calculate the concentrations of each of the many species present at equilibrium under given conditions of temperature, total pressure, and total chemical NO and NO_2 concentrations. This "equilibrium model" was necessary since not every species could be measured.

In summary, it was found that a mechanism for NO_x sorption from flue gases had to be proposed on the basis of chemical composition and total concentration. An "equilibrium model" was therefore needed to (1) give a detailed description of the equilibrium composition at a given temperature, pressure and total concentration, and (2) allow a description of the changing composition as nitrogen species were transferred from

the gas to the aqueous phase. The proposed mechanism then had to be tested in experiments in which sufficient data were collected to calculate material balances with the help of the equilibrium model.

3.3 Summary of Problem Definition

The problem of removing NO and NO_2 from flue gases by aqueous sorption has not heretofore been completely defined. The scope of the problem as it was investigated by Radian was narrowed by the following factors:

- 50 ppm NO_2 and 450 ppm NO had to be removed from flue gas also containing about 13% CO_2.
- While the primary goal was to obtain a theoretical description of NO and NO_2 sorption in a wet scrubber, the theoretical description was developed for a complete process, i.e., not just the scrubbing step. Two processes, a "dry" and an aqueous process, were investigated.
- The theoretical description had to be used to evaluate the performance of potential dry metal oxide sorbents in the process of interest.

To properly define the problem whose scope was described above, the following questions had to be answered:

- What nitrogen-containing oxide species are present in the flue gas; what aqueous species are formed by sorption; and what reactions take place in the system ?

- What is the mechanism for the sorption process and which of the steps controls the rate of sorption from gas mixtures having the composition and concentration of flue gases?

The answer to the first question was found from the chemical literature. The second question had not been previously investigated. Research had been conducted on related problems and some of the ideas could be applied to aqueous sorption from flue gases. It was found that to fully define the problem two things were needed:

- an equilibrium model which would allow the concentration of each of the many species present at equilibrium to be calculated,

- experimental studies to verify a proposed sorption mechanism. The equilibrium model would also be required to perform some aspects of the mass balance and mass transfer calculations.

4.0 THE COMPOSITION-CONCENTRATION MODEL

From the process of defining the problem for development of a theoretical description of aqueous scrubbing of NO_x from flue gases, the complexity of the nitrogen oxides-water system became apparent. It was then obvious that a basic description of the system required that the concentrations of each of the gaseous and aqueous species present be known. It was recognized that some species might be present in concentrations too small to be of significance for a mass balance. At the same time, if the species present in relatively small concentrations were involved in the rate controlling step for sorption, then it would be necessary to know their concentration and how it changes as sorption occurs. A knowledge of the relative concentrations of the gas phase species was also needed in order to predict which compound of nitrogen and oxygen would be involved in the rate-limiting step for mass transfer.

While the gas phase NO_x-H_2O system is quite complicated, the aqueous phase system presents an even greater problem since ionization creates a greater number of possible reactants and reaction pathways. In addition, concentrations of the ionic species suggested to be involved in aqueous phase rate limiting steps are more difficult to measure. Waldorf (WA-015) has studied the application of ultraviolet spectroscopy to the identification of many of the ionic and molecular aqueous phase species, but routine analytical methods have not yet been developed. Evaluation of the relative rates of different reaction pathways to determine which might be rate limiting presents a formidable task. Finally, the aqueous solutions of interest for this problem are of relatively high ionic strength and are far from ideal solutions. Calculations must therefore be based on activities rather than measured molalities. Radian

has previously developed an aqueous equilibrium model which describes ionic interactions in scrubbing liquors for SO_2 removal processes. The model calculates activity coefficients from ionic strength and takes into account the equilibria of ion-ion interactions; therefore, it is applicable to the non-ideal solutions involved in NO_x sorption. The physical and thermochemical data for some molecular and ionic nitrogen-oxygen species were added to the existing aqueous model. [The data are described in Technical Note 200-007-11 (Volume II) and in Section 8.0 of this report.] However, since the kinetics of liquid phase reactions for NO_x sorption have not yet been fully defined, it is not known whether the aqueous equilibrium model will be sufficient for describing aqueous phase interactions in NO_x sorption processes.

The same problems do not exist for the gas mixture. The species present other than NO, NO_2, H_2O and their reaction products act as inerts so that the system is effectively quite dilute. At the temperatures and low NO + NO_2 pressures which prevail the gases almost obey the ideal gas law (PV = RT). Fugacity coefficients are almost unity. Half times of some of the gas phase reactions were reported in the literature to be on the order of centiseconds (WA-016) and microseconds (CA-069). Other reactions were described as instantaneous (WA-016). The reactions are considered to have reached equilibrium within scrubber gas residence times. A description of the relative concentrations of the gas phase species at equilibrium was selected as a useful and logical starting point. Accordingly, a gas phase equilibrium model was developed. It is described in this section and in detail in Technical Note 200-007-03a, included in Volume II of the report. A listing of the computer subroutines written to calculate the gas phase equilibrium concentrations is also included in Volume II in Technical Note 200-007-16.

4.1 Reactions Considered in the Gas Phase Equilibrium Model

In Section 3.2.1, Table 3-3, the gas phase species in the NO_x-H_2O system were listed, and some equations were given to describe their interactions. The selection of the reactions used to describe equilibrium in the gas phase is documented in Technical Note 200-007-03a (Volume II of this report). The selected reactions are given in equations (4-1) through (4-5).

$$NO + NO_2 \rightleftarrows N_2O_3 \quad (4\text{-}1)$$

$$2NO_2 \rightleftarrows N_2O_4 \quad (4\text{-}2)$$

$$N_2O_3 + H_2O \rightleftarrows 2HNO_2 \quad (4\text{-}3)$$

$$N_2O_4 + H_2O \rightleftarrows HNO_2 + HNO_3 \quad (4\text{-}4)$$

$$NO + N_2O_5 \rightleftarrows NO_2 + N_2O_4 \quad (4\text{-}5)$$

There is little question that the reactions in (4-1), (4-2) and (4-3) are equilibrium reactions (CH-032, p.55; WA-014; WA-015, pp. 11-12; WA-016). There is great controversy concerning whether nitric acid is formed in a homogeneous gas phase reaction such as (4-4). The facts presented to date are discussed in detail in the technical note. Reaction (4-5) was included so that equilibrium partial pressures of N_2O_5 could be calculated. The reaction for oxidation of NO to NO_2 was not included in the equilibrium formulation since it would not reach equilibrium within gas residence times in the scrubber. The half time for the oxidation reaction is about 21 minutes at scrubber conditions of 43°C, 8 mole % oxygen and .05 mole % NO. Under the same conditions, about 1% would be oxidized after 5 seconds.

4.2 Problem Formulation and Method of Solution

The purpose of the gas phase equilibrium model was to calculate the partial pressure or mole fraction of each of the

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4.2 Problem Formulation and Method of Solution

The purpose of the gas phase equilibrium model was to calculate the partial pressure or mole fraction of each of the

gaseous species present at equilibrium under given conditions of total pressure and temperature. A computer program was written to perform the calculations.

There are eight components for which the mole fraction was to be calculated. These eight unknowns are calculated from a system of eight nonlinear equations. The eight nonlinear equations consist of five equations for the equilibrium constants of the reactions in (4-1) through (4-5) plus three mass balance equations. The mass balance equations are defined in (4-6), (4-7) and (4-8), where n is the number of moles of each component, N_T is the total number of moles, and y is the mole fraction of each component.

Chemical NO

$$C_{NO} = n_{NO} + n_{N_2O_3} + \tfrac{1}{2}n_{HNO_2} - \tfrac{1}{2}n_{HNO_3} - n_{N_2O_5}$$

$$= N_T \left(y_{NO} + y_{N_2O_3} + \tfrac{1}{2}y_{HNO_2} - \tfrac{1}{2}y_{HNO_3} - y_{N_2O_5}\right) \quad (4\text{-}6)$$

Chemical NO_2

$$C_{NO_2} = n_{NO_2} + 2n_{N_2O_4} + n_{N_2O_3} + \tfrac{1}{2}n_{HNO_2} + 3/2n_{HNO_3} + 3n_{N_2O_5}$$

$$= N_T \left(y_{NO_2} + 2y_{N_2O_4} + y_{N_2O_3} + \tfrac{1}{2}y_{HNO_2} + 3/2y_{HNO_3} + 3y_{N_2O_5}\right) \quad (4\text{-}7)$$

Chemical H_2O

$$C_{H_2O} = n_{H_2O} + \tfrac{1}{2}n_{HNO_2} + \tfrac{1}{2}n_{HNO_3}$$

$$= N_T \left(y_{H_2O} + \tfrac{1}{2}y_{HNO_2} + \tfrac{1}{2}y_{HNO_3}\right) \quad (4\text{-}8)$$

Chemical NO, NO_2, and H_2O are inputs to the program. They are quantities which can be measured. The mass balance equations describe the distribution of the total number of moles among the possible molecular species. Chemical NO is the term used to describe the number of moles of nitrogen in the +2 oxidation state as shown in Equation 4-6. Chemical NO_2 describes the number of moles of nitrogen in the +4 oxidation state, Equation 4-7. The mass balance equations were derived by considering the stoichiometry of Equations 4-1 through 4-5. For example, since one mole of NO is used in the formation of a mole of N_2O_3, the term $n_{N_2O_3}$ is included in the mass balance equation for +2 nitrogen. One mole of N_2O_3 contains one mole of NO and forms two moles of HNO_2 (Equation 4-3). However, some HNO_2 is also formed from +4 nitrogen according to Equation 4-4. The total number of moles of HNO_2 formed is shown as follows:

$$n_{HNO_2\,(TOTAL)} = n_{HNO_2\,(4-3)} + n_{HNO_2\,(4-4)} \qquad (4-9)$$

We would like to include the term $\frac{1}{2}n_{HNO_2\,(4-3)}$ in the +2 nitrogen balance but it is impossible to distinguish between the HNO_2 formed according to Equation 4-3 and that formed as in Equation 4-4. Only $n_{HNO_2\,(TOTAL)}$ is known. However, the amount of HNO_2 formed according to Equation 4-4 is equal to the amount of HNO_3 formed:

$$n_{HNO_2\,(4-4)} = n_{HNO_3\,(4-4)} = n_{HNO_3\,(TOTAL)} \qquad (4-10)$$

Since this is the only path by which HNO_3 is formed in the Radian formulation, the amount of HNO_2 formed according to Equation 4-3 can be indicated by substituting $n_{HNO_3\,(4-4)}$ for $n_{HNO_2\,(4-4)}$:

$$n_{HNO_2\,(TOTAL)} = n_{HNO_2\,(4-3)} + n_{HNO_3\,(4-4)} \qquad (4-11)$$

and

$$n_{HNO_2}(4\text{-}3) = n_{HNO_2}(\text{TOTAL}) - n_{HNO_3}(4\text{-}4)$$
$$= n_{HNO_2} - n_{HNO_3} \qquad (4\text{-}12)$$

Therefore the term $\frac{1}{2}n_{HNO_2}(4\text{-}3)$ can be replaced by $\frac{1}{2}n_{HNO_2} - \frac{1}{2}n_{HNO_3}$ in the +2 nitrogen balance.

The five equilibrium constant equations are the nonlinear ones. They are expressed in terms of total pressure, mole fractions of products and reactants and fugacity coefficients The total pressure is a program input. The equilibrium constants themselves are calculated as a function of temperature from standard state thermodynamic properties and heat capacities The equilibrium constant temperature dependence data are stored by the program and the temperature is a program input. As mentioned previously, the fugacity coefficients are very nearly unity since the gas mixture is effectively an ideal gas.

The system of eight nonlinear equations is solved in the logarithmic domain using an iterative procedure originally developed for calculating aqueous solution equilibria (LO-007).

4.3 Comparison of Calculated and Measured Results

A concentrated effort was made to compare measured and calculated values of the mole fractions or partial pressures present at equilibrium in the NO_x-H_2O vapor phase system. The effort is described in detail in Technical Note 200-007-03a. An experimental program to measure gas phase equilibrium concentrations was beyond the scope of Contract EHSD 71-5. Therefore,

it was necessary to rely on published measurements of equilibrium concentrations. The only measured equilibrium concentrations reported in the literature were for the component NO_2. A thorough search revealed that analytical methods do not exist for some of the species and the few existing methods for the other species have not been applied to equilibrium mixtures. The comparison of some measured and calculated NO_2 partial pressures is shown in Table 4-1 and a comparison of measured and calculated total number of moles, N., is shown in Table 4-2.

TABLE 4-1

COMPARISON OF CALCULATED AND MEASURED PARTIAL PRESSURES OF NO_2

Temperature °C	P_{NO_2} (atm)		
	Calculated	Measured	Reference
29.95	.0227	.0204	AS-004
25.04	.073	.067	VO-007
	.053	.050	
	.032	.031	
	.018	.017	
80.7	.0263	.0233	AS-004

TABLE 4-2

COMPARISON OF CALCULATED AND MEASURED TOTAL NUMBER OF MOLES

Temperature °C	N_T Calculated by Equilibrium Program	N_T Calculated from Measured Total Pressure (BE-023)
25.04	.0358	.0353
25.04	.0345	.0341
25.04	.0395	.0391
45.12	.0144	.0152
45.04	.0452	.0463

4.4 Application of the Gas Phase Equilibrium Model to Predict the Rate Controlling Step

Table 4-3 shows the results obtained when the gas phase equilibrium model was used to calculate the mole fractions of NO, NO_2, N_2O_3, N_2O_4, HNO_2 and HNO_3 present at flue gas scrubber conditions of 60°C, 1 atmosphere total pressure, and 8 mole % H_2O. The calculations were made to demonstrate the effect of total concentration of input chemical NO + NO_2 and the effect of relative concentrations of input chemical NO and NO_2 on the equilibrium concentrations. Additional calculations were performed to determine the effect of temperature and total pressure on the equilibrium distribution, and they were found to have a negligible effect on the relative distributions.

The calculated equilibrium concentrations can be used to explain which compounds should be involved in the rate limiting step for nitrogen oxides absorption at different gas compositions and concentrations. Investigators studying absorption of

TABLE 4-3

EQUILIBRIUM COMPOSITIONS IN THE GAS PHASE SYSTEM

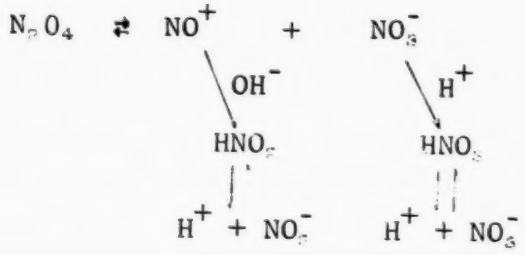
NO_x-H_2O AT 60°C, 1 ATM TOTAL PRESSURE, AND 8 MOLE % H_2O

Total Input Concentrations $NO+NO_2$ (mole%)	Relative Concentrations Input NO and NO_2	Equilibrium Concentrations (mole fraction)					
		NO	NO_2	N_2O_3	N_2O_4	HNO_2	HNO_3
.05	Equimolar	2.43×10^{-4}	2.37×10^{-4}	5.33×10^{-9}	3.99×10^{-8}	1.70×10^{-5}	2.71×10^{-6}
	10% NO_2, 90% NO	4.45×10^{-4}	4.48×10^{-5}	1.84×10^{-9}	1.42×10^{-9}	9.99×10^{-6}	1.64×10^{-7}
	90% NO_2, 10% NO	5.18×10^{-5}	4.23×10^{-4}	2.03×10^{-9}	1.27×10^{-7}	1.05×10^{-5}	1.40×10^{-5}
.5	Equimolar	2.43×10^{-3}	2.37×10^{-3}	5.31×10^{-7}	3.97×10^{-8}	1.70×10^{-4}	2.7×10^{-5}
	10% NO_2, 90% NO	4.45×10^{-3}	4.47×10^{-4}	1.84×10^{-7}	1.42×10^{-7}	9.98×10^{-5}	1.64×10^{-6}
	90% NO_2, 10% NO	5.17×10^{-4}	4.21×10^{-3}	2.01×10^{-7}	1.26×10^{-5}	1.04×10^{-4}	1.39×10^{-4}
1.0	Equimolar	4.85×10^{-3}	4.72×10^{-3}	2.12×10^{-6}	1.58×10^{-5}	3.38×10^{-4}	5.36×10^{-5}
	10% NO_2, 90% NO	8.9×10^{-3}	8.94×10^{-4}	7.35×10^{-7}	5.65×10^{-7}	1.99×10^{-4}	3.27×10^{-6}
	90% NO_2, 10% NO	1.03×10^{-3}	8.38×10^{-3}	8.0×10^{-7}	4.98×10^{-5}	2.08×10^{-4}	2.75×10^{-4}
2.0	Equimolar	9.71×10^{-3}	9.37×10^{-3}	8.41×10^{-6}	6.22×10^{-5}	6.73×10^{-4}	1.06×10^{-4}
	10% NO_2, 90% NO	1.78×10^{-2}	1.78×10^{-3}	2.93×10^{-6}	2.25×10^{-6}	3.98×10^{-4}	6.51×10^{-6}
	90% NO_2, 10% NO	2.06×10^{-3}	1.66×10^{-2}	3.16×10^{-6}	1.95×10^{-4}	4.12×10^{-4}	5.42×10^{-4}
5.0	Equimolar	2.42×10^{-2}	2.30×10^{-2}	5.16×10^{-5}	3.75×10^{-4}	1.66×10^{-3}	2.57×10^{-4}
	10% NO_2, 90% NO	4.45×10^{-2}	4.43×10^{-3}	1.82×10^{-5}	1.39×10^{-5}	9.91×10^{-4}	1.61×10^{-5}
	90% NO_2, 10% NO	5.12×10^{-3}	4.02×10^{-2}	1.91×10^{-5}	1.15×10^{-3}	1.01×10^{-3}	1.29×10^{-3}
10.0	Equimolar	4.84×10^{-2}	4.46×10^{-2}	2.0×10^{-4}	1.41×10^{-3}	3.26×10^{-3}	4.89×10^{-4}
	10% NO_2, 90% NO	8.90×10^{-2}	8.79×10^{-3}	7.23×10^{-5}	5.47×10^{-5}	1.97×10^{-3}	3.17×10^{-5}
	90% NO_2, 10% NO	1.02×10^{-2}	7.69×10^{-2}	7.26×10^{-5}	4.21×10^{-3}	1.96×10^{-3}	2.42×10^{-3}
50.0	Equimolar	2.39×10^{-1}	1.85×10^{-1}	4.26×10^{-3}	2.83×10^{-2}	1.44×10^{-2}	1.82×10^{-3}
	10% NO_2, 90% NO	4.44×10^{-1}	4.10×10^{-2}	1.70×10^{-3}	1.20×10^{-3}	9.30×10^{-3}	1.40×10^{-4}
	90% NO_2, 10% NO	4.85×10^{-2}	2.97×10^{-1}	1.44×10^{-3}	6.76×10^{-2}	8.37×10^{-3}	8.34×10^{-3}

concentrated gas mixtures containing mostly NO_2 found the removal rate proportional to the concentration of N_2O_4. The equilibrium concentrations for the case of 50 mole % chemical NO + NO_2 input concentration and composition 90% NO_2 - 10% NO are (in mole fractions):

NO_2	N_2O_4	NO	HNO_2	HNO_3	N_2O_3
.297	.0676	.0485	.00837	.00834	.00144

The properties which affect the rate at which a molecule can be absorbed are its diffusivity, solubility, chemical reactivity in the aqueous phase, and relative concentration and diffusivity in the gas phase. The diffusivities of all these species are of the same order of magnitude, so that property probably doesn't significantly affect the absorption rate. Nitric oxide, NO, is the least soluble of the species. In fact, its solubility is so small that even if equilibrium conditions existed for NO dissolution, the amount of nitric oxide removal observed would not be accounted for by mass transfer of NO. The other species: NO_2, N_2O_3, N_2O_4, HNO_2 and HNO_3 then remain as candidates for participant in the mass transfer mechanism and rate limiting step. The aqueous phase chemical reactivities and relative gas phase concentrations remain as properties which influence the rate of sorption. The relative concentrations are shown above in descending order. Clearly NO_2 and N_2O_4 are present in concentrations orders of magnitude greater than HNO_2, HNO_3 and N_2O_3. The fact that the absorption rate in gas mixtures of this type was found to be proportional to the concentration of N_2O_4 rather than NO_2 must then be due to the fact that N_2O_4 is much more chemically reactive than NO_2 in aqueous solutions. The greater reactivity could be accounted for by greater ease of ionization for N_2O_4 than for NO_2. Indeed, the proposed mechanism for reaction of NO_2-N_2O_4 mixtures with water (MO-008, p. 20; WA-015, p. 18; and KO-026, p. 32) involves the sequence of reactions in equation (4-9).



(4-9)

Now that it has been shown how equilibrium concentrations can be used to determine mass transfer mechanism and rate limiting step for a known case, let us consider the unknown case of sorption from flue gas mixtures. From Table 4-3, the calculated equilibrium concentrations for a gas mixture containing .05 mole % NO + NO_2 composed of 90% NO and 10% NO_2 are as follows (mole fractions x 10^4):

NO	NO_2	HNO_2	HNO_3	N_2O_3	N_2O_4
4.45	.448	.0999	.00164	.0000184	.0000142

Consideration of solubilities and relative gas phase concentrations shows clearly that NO, N_2O_4, and N_2O_5 could not be the species for describing mass transfer or rate limiting step. Again NO is too insoluble to account for the amount of NO sorbed. Because the vapor phase diffusivities of HNO_2, HNO_3, N_2O_3 and N_2O_5 are almost equal, the vapor film coefficients for all of these species are almost equal. The relative amounts of mass transfer for the various species will depend on the relative value of the driving forces (concentrations). The concentrations of HNO_2 and HNO_3 are orders of magnitude greater than N_2O_3 or N_2O_5. For the liquid film the diffusivities of the unionized species are approximately equal. The solubilities of HNO_2 and HNO_3 would be expected to be larger than N_2O_3 or N_2O_5 because of the rapid ionization rates of HNO_2 and HNO_3 as compared to the rates of the chemical reactions for N_2O_3 and N_2O_4. Therefore every step in the mass transfer sequence is faster for HNO_2 and HNO_3 than for N_2O_3 or N_2O_5. Obviously the mechanisms proposed for absorption from gas mixtures

of the concentration and composition typical of nitric acid plant tail gases do not apply to this case.

The species remaining to be considered are then NO_2, HNO_2, and HNO_3. Although NO_2 is present in much greater gas phase concentrations than HNO_2 or HNO_3, there is reason to believe that it does not react rapidly in the aqueous phase until it has dimerized to form $N_2O_{4(\ell)}$ after which subsequent ionization, hydrolysis, and ionization steps (equation 4-9) must take place before nitrite and nitrate are formed. However, HNO_2 and HNO_3 do not have to react further once they are dissolved in the aqueous phase. Only one ionization step has to take place before nitrate and nitrite are formed. Furthermore, if NO_2 diffusion and reaction were the only mechanism, nitrite and nitrate would be formed in equimolar quantities in the aqueous phase, which is not the case. The conclusion is that HNO_2 and HNO_3 must be the species through which significant mass transfer takes place during sorption from flue gas mixtures since they offer the path of least resistance. The steps involved in HNO_2 and HNO_3 mass transfer are bulk gas diffusion, gas film diffusion, liquid film diffusion and ionization in the bulk liquid. The slowest of these steps is probably gas film diffusion, so that the proposed mechanism and rate controlling step is gas film limited diffusion of HNO_2 and HNO_3. It is also possible that the aqueous phase reactions in Equation 4-10

$$NO_{2(\ell)} \rightleftarrows N_2O_{4(\ell)} \rightleftarrows NO^+ + NO_3^- \xrightarrow{H_2O} HNO_2 + HNO_3 \rightleftarrows 2H^+ + NO_2^- + NO_3^- \qquad (4\text{-}10)$$

are so fast that both the gas phase acids and NO_2 contribute to the mechanism. The next step was to investigate these possibilities using experimental methods.

5.0 EXPERIMENTAL PROGRAM

It is clear from the problem definition that insufficient physical and thermochemical data exist to enable one to verify the predicted mass transfer mechanism and rate limiting step for NO_x aqueous sorption from flue gas mixtures. The usual practice is to verify the predictions experimentally. An experimental program was not included in the scope of work of Contract EHSD 71-5. However, an inhouse experimental program at the OAP Laboratory Research Branch Cincinnati laboratories was being carried out during the period of contract performance. The sorption of equimolar NO-NO_2 mixtures in a variety of aqueous sorbents was under investigation. In order that the inhouse program might receive the full benefit of Radian theoretical studies, a contract modification was made according to which Radian would cooperate closely with the existing experimental program in an effort to verify the mass transfer mechanism. Much valuable experience was gained as a result of the close cooperation that was possible. Most of the experimental results were obtained before the time that Radian became closely involved with the program. These results were reported by Garcia (GA-046) at the Second International Lime/Limestone Wet Scrubbing Symposium. Radian participated directly in data collection and analysis for only three experiments. Much additional experience was obtained through discussions about the experimental apparatus and the data obtained in experiments in which Radian was not directly involved. In section 5 the apparatus is described, but only the raw data obtained specifically for Radian are presented. In addition, the practical experience gained through cooperation with the experimental program is discussed. In section, 6.0, an engineering analysis of the data collected during Radian participation is described.

5.1 Apparatus and Data Collected

A flow diagram of the experimental apparatus used in OAP inhouse studies is shown in Figure 5-1. The apparatus was modified slightly during the experiments in which Radian participated, since the object of these experiments differed from the general goals of the inhouse program. Instead of using a simulated flue gas produced by combustion of methane in air and addition of SO_2 and NO_2, the inlet gas was a mixture of NO and NO_2 in nitrogen. The entering gas stream was not preheated. The scrubber was a 2¼-inch ID glass column packed with 18 inches of 3/8-inch Berl saddles. The measured gas flow rates were corrected for pressure drop and density. Using the measured gas and liquid flows, IR and UV analyses for chemical NO and chemical NO_2, respectively, in the entering and effluent gas, and UV analysis for nitrite and nitrate in scrubbing liquid and condensate, the data shown in Table 5-1 were calculated. A detailed description of the material balance calculations is given in Technical Note 200-007-09, which is included in Volume II of this report.

5.2 Practical Experience Gained

Experience gained by OAP and Radian investigators during the study of aqueous sorption of nitrogen oxides revealed the difficulties involved in calculating material balances and mass transfer coefficients in a system as complicated as the NO_x-H_2O system.

FIGURE 5-1

FLOW DIAGRAM OF EQUIPMENT
USED IN EPA IN-HOUSE EXPERIMENTS

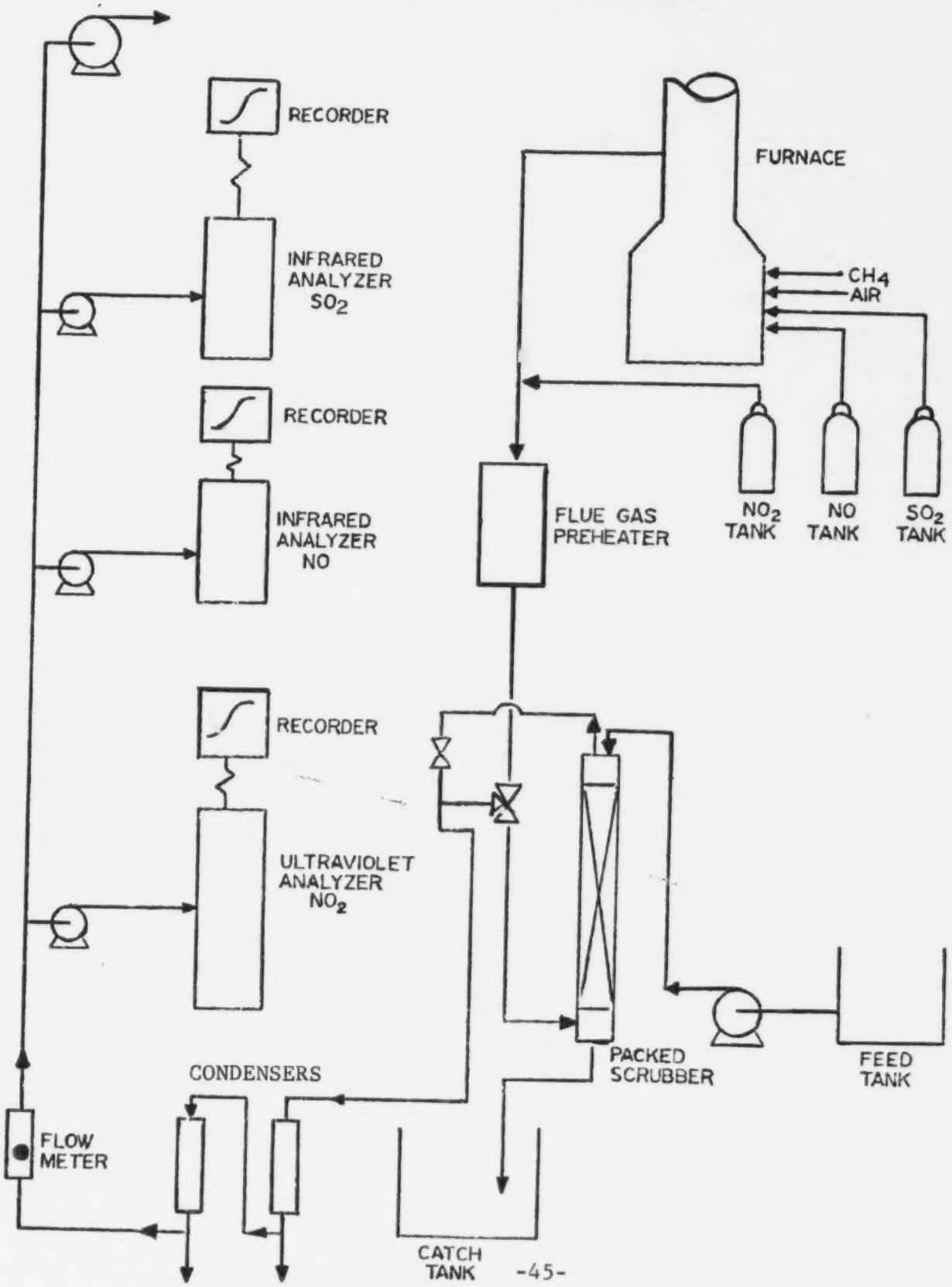


TABLE 5-1

SUMMARY OF DATA COLLECTED AT EPA LABORATORY, MAY 1971

(Moles/min x 10^6)

		In	Out		
Run No.		Entering Gas	Exit Gas	Scrubber Liquid	Condensate
1	C_{NO}*	102.76	97.54	21.14	**
	C_{NO_2}	101.03	52.84	60.08	
2	C_{NO}	135.60	134.05	21.72	-3.2
	C_{NO_2}	130.80	68.79	62.95	9.0
3	C_{NO}	172.80	185.12	23.61	
	C_{NO_2}	162.00	85.95	70.56	

*C_{NO} and C_{NO_2} refer to chemical NO and chemical NO_2 as defined in the mass balance equations in the problem definition.

**Analysis conducted only for Run 2.

Since there are many possible compounds of nitrogen and oxygen and several oxidation states that are exhibited by the nitrogen, it is important either to exclude or to account for the possibility of oxidation. This factor was even more important for the method of data analysis employed in this study. The material balance equations were based on conservation of the +4 and +2 oxidation states of nitrogen. Therefore, experiments to verify the mass transfer mechanism had to be performed in an atmosphere of nitrogen rather than air or oxygen.

Second, it is necessary but quite difficult in practice to obtain starting materials of known purity. It was found that one commercial NO-N_2 cylinder contained about 25% NO_2. An oversight of such an impurity would lead to obvious difficulties in data analysis.

Difficulties in chemical analysis, as first pointed out in the problem definition from literature reports, were confirmed during the experimental studies. Some of these problems were solved satisfactorily. It was found that at elevated temperatures, less than 1% of the nitrogen-oxygen species present exist in molecular forms other than NO and NO_2. Therefore, if analytical measurements are conducted at elevated temperatures, the molecular NO and NO_2 concentrations are essentially equal to the chemical NO and chemical NO_2 required as inputs to the equilibrium model. The relative concentrations of other gas phase molecules can then be calculated by the equilibrium model at the lower temperatures of interest.

The fact that water vapor interferes in the gas phase analyses was not solved satisfactorily. The method used to eliminate the interference was the application of two water-cooled condensers. Unfortunately, some of nitrogen oxides are

removed in the condensate along with the water vapor. The problem was circumvented by chemical analysis of the condensate for nitrite and nitrate.

6.0 ENGINEERING ANALYSIS OF SORPTION DATA

Insufficient data were taken and not a wide enough range of vapor and liquid rates was investigated to prove or disprove the proposed mass transfer mechanism or to provide a correlation that can be applied with confidence. The limited amount of data was analyzed on the basis of vapor film limited mass transfer of HNO_2 and HNO_3, and mass transfer coefficients for HNO_2 and HNO_3 were calculated which can be applied for vapor rates of from 0.7 to 1.2 normal meter^3/hr. No attempt was made to account for the influence of NO_2 mass transfer.

6.1 Problem Formulation

The data analysis procedure differs slightly from standard methods of calculating mass transfer coefficients since the species being removed from the gas phase, HNO_2 and HNO_3, are not conserved, i.e., sorbed HNO_2 and HNO_3 are quickly replaced due to the reactions between N_2O_3, N_2O_4 and H_2O.

The problem formulation is given in detail in Technical Note 200-007-12, included in Volume II of this report. It is summarized in the following paragraphs. An expression for the number of moles of HNO_2 or HNO_3 transferred in a differential height of packing, dz, of crossectional area A_c is given in equation (6.1).

$$-dn_x = k_x a A_c P(y_x - y_x^*)dz \qquad (6\text{-}1)$$

The subscript x refers to HNO_2 (x = 1) or HNO_3 (x = 2). P is the total pressure, a is the surface area of packing per unit volume, k is the mass transfer coefficient, and y is the mole fraction in the bulk gas. Assuming the equilibrium partial

pressure over the liquid, y*, is zero results in equation (6-2).

$$-dn_x = k_x a A_c P y_x \, dz \qquad (6\text{-}2)$$

The quantities that can be measured in sorption experiments are chemical NO C_{NO} and chemical NO_2 C_{NO_2}. These quantities were defined by the mass balance equations in equations (4-6) and (4-7). The change in the number of moles of chemical NO and NO_2 corresponding to the change in number of moles of HNO_2 and HNO_3 are therefore shown in equations (6-3) and (6-4) from the mass balance equations.

$$dC_{NO} = \tfrac{1}{2}(dn_{HNO_2} - dn_{HNO_3}) \qquad (6\text{-}3)$$

$$dC_{NO_2} = \tfrac{1}{2}(dn_{HNO_2} + 3dn_{HNO_3}) \qquad (6\text{-}4)$$

Substituting (6-2) into (6-3) and (6-4) gives (6-5a) and (6-5b) where α_1 is $k_{HNO_2} a P A_c$ and α_2 is $k_{HNO_3} a P A_c$.

$$-dC_{NO} = \tfrac{1}{2}(\alpha_1 y_{HNO_2} - \alpha_2 y_{HNO_3})dz \qquad (6\text{-}5a)$$

$$-dC_{NO_2} = \tfrac{1}{2}(\alpha_1 y_{HNO_2} + 3\alpha_2 y_{HNO_3})dz \qquad (6\text{-}5b)$$

The amount of chemical NO_2 and NO removed in a column of height H can then be calculated by numerically integrating (6-5a) and (6-5b). Values for α_1 and α_2 are then calculated such that the difference between the amount removed calculated using (6-5a) and (6-5b) and the measured amount removed is minimized. A computer program was written to perform the calculations. It utilizes the gas phase equilibrium model subroutine for calculating mole fractions of HNO_2 and HNO_3 for

given chemical NO and NO_2, pressure, and temperature. A first guess for σ_1 and σ_2 is obtained by calculating mass transfer coefficients for HNO_2 and HNO_3. The first trial mass transfer coefficients were calculated using a correlation for the vapor film coefficient for the ammonia-water system (BR-002, p. 530) and correcting for the difference in diffusivities.

6.2 Data Used in Correlation

The data shown in Table 5-1 were used in the correlation for calculating mass transfer coefficients. The measurements of gas phase concentrations were not as accurate as the results of the liquid phase chemical analyses. Therefore, the data were recalculated to place more emphasis on the most accurate measurements. An "average" inlet concentration, $In_{avg.}$ was recalculated. All of the inlet C_{NO} and C_{NO_2} entered in the gas. The C_{NO} and C_{NO_2} left in both the gas and the liquid streams. The material balance can then be represented by equation (6-6).

$$In_{gas} = Out_{gas} + Out_{liquid} \tag{6-6}$$

Although In_{gas}, Out_{gas}, and Out_{liquid} were all measured, the liquid phase measurements are the ones in which one should have the most confidence. Therefore, the inlet concentration was recalculated as shown in equation (6-7).

$$2(In_{avg}) = In_{gas} + Out_{gas} + Out_{liquid}$$

or

$$In_{avg} = \tfrac{1}{2}(In_{gas} + Out_{gas} + Out_{liquid}) \tag{6-7}$$

The recalculated outlet concentration is shown in equation (6-8).

$$Out_{avg,gas} = In_{avg} - Out_{liquid} \qquad (6\text{-}8)$$

The values for In_{avg} and $Out_{avg,gas}$ used in the correlation were calculated from the data in Table 5-1. They are shown in Table 6-1.

TABLE 6-1

RECALCULATED VALUES OF C_{NO} AND C_{NO_2} IN THE INLET AND EFFLUENT GAS IN NO_x SORPTION EXPERIMENTS

		Gas In (moles/min x 10^6)	Gas Out (moles/min x 10^6)
Run 1	C_{NO}	110.72	89.58
	C_{NO_2}	106.97	46.89
Run 2	C_{NO}	144.10	122.38
	C_{NO_2}	135.75	72.80
Run 3	C_{NO}	190.75	167.14
	C_{NO_2}	159.25	88.69

6.3 Results

The vapor film coefficients for HNO_2 and HNO_3 calculated as described in Section 6.1 with the data given in Section 6.2 are shown in Table 6-2.

TABLE 6-2

RESULTS OF MASS TRANSFER COEFFICIENT CALCULATIONS

Run No.	Vapor Flow Rate $\left[\frac{\text{normal } M^3}{\text{hour}}\right]$	Liquid Rate $\left[\frac{cm^3}{min}\right]$	$K_g a_{HNO_2}$ $\left[\frac{\text{gm mole}}{(hr)(cm^3)(atm)}\right]$	$K_g a_{HNO_3}$ $\left[\frac{\text{gm mole}}{(hr)(cm^3)(atm)}\right]$
1	0.728	710	0.277	0.972
2	0.948	710	0.275	0.962
3	1.18	710	0.302	1.22

The vapor and liquid rate dependence of the coefficients can be described by equations (6-9) and (6-10).

$$k_g a_{HNO_2} = 0.795 \left(\frac{V}{A_c}\right)^{0.8} \left(\frac{L}{A_c}\right)^{0.39} \qquad (6\text{-}9)$$

$$k_g a_{HNO_3} = 2.96 \left(\frac{V}{A_c}\right)^{0.8} \left(\frac{L}{A_c}\right)^{0.39} \qquad (6\text{-}10)$$

These equations and this mechanism must be considered as being tentative. The ratio of $k_g a_{HNO_2} / k_g a_{HNO_3}$ is 0.27 and not 1.04 as predicted by film theory. This could be explained by inaccuracy of equilibrium constants used to calculate mole fractions of HNO_2 or HNO_3.

7.0 SCREENING OF CANDIDATE SORBENTS ON THE BASIS OF THE THERMODYNAMICS OF THE SORPTION REACTIONS

The ultimate goal of this study was to develop a theoretical description of aqueous scrubbing and to use the theoretical description for two purposes:

- to satisfy some of the engineering requirements of new process development
- to predict the most effective and efficient sorbents for use in the process.

This section describes how candidate sorbents were screened for effectiveness in two different processes for NO_x removal. Screening was conducted on the basis of the thermodynamics of the reactions between nitrogen oxides and the candidate sorbent.

7.1 Description of the Processes for which Candidate Sorbents were Screened

The metal oxide sorbents considered for applicability in NO, removal processes are listed in Table 7-1. Two processes were considered: a dry process and an aqueous process. Both start with dry metal oxides and result in the formation of solid metal nitrites and/or nitrates as end products.

The processes are regenerative. Regeneration could be accomplished either by temperature, pressure, or chemical changes. One example of a method for regenerating the starting

TABLE 7-1

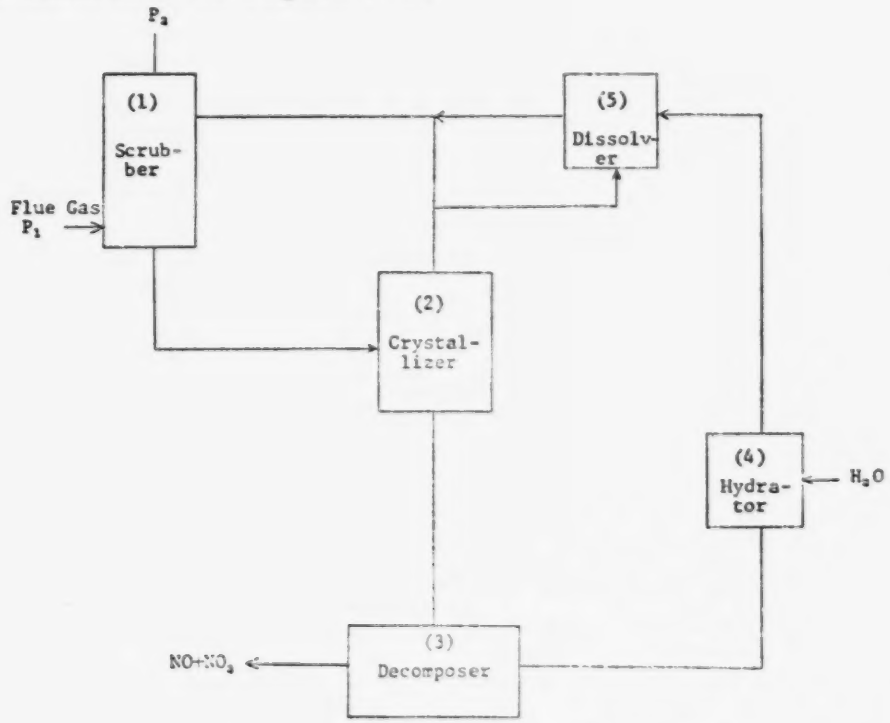
METAL OXIDES SCREENED FOR APPLICABILITY IN NO_x REMOVAL PROCESSES

Ag_2O	Fe_2O_3
Al_2O_3	K_2O
BaO	Li_2O
BeO	MgO
Bi_2O_3	MnO
CaO	Mn_2O_3
CdO	Na_2O
CeO_2	NiO
CoO	PbO
Cu_2O	SnO_2
CuO	SrO
FeO	ZnO
	ZrO_2

material is thermal decomposition. Many metal nitrites or nitrates can be thermally decomposed at temperatures of several hundred °C to yield the starting material metal oxide and gaseous nitrogen oxides. The published data on thermal decomposition of nitrites and nitrates are summarized in Technical Note 200-007-06 (see Volume II).

The dry process under consideration involves sorption of gaseous nitrogen-oxygen compounds on dry metal oxides to form metal nitrates and/or nitrites. Regeneration of the sorbent is by thermal decomposition of the sorption products. The gaseous nitrogen compounds are to be removed from a flue gas containing both water vapor and CO_2 so that formation of carbonates and hydroxides must also be considered.

The aqueous process for which screening was carried out is described in Figure 7-1.



FLOW DIAGRAM FOR AQUEOUS PROCESS
FIGURE 7-1

The process shown in Figure 7-1 involves the following steps:

1. hydration of the metal oxide to form the hydroxide

2. dissolution of the hydroxide

3. sorption of gaseous nitrogen oxide species from flue gas containing $CO_{2(g)}$, and $H_2O_{(g)}$ into the aqueous solution

4. crystallization of nitrates and/or nitrites

5. thermal decomposition of the nitrates and/or nitrites to regenerate the dry metal oxide.

One aspect of the screening procedure should be emphasized. The material or chemicals that were selected as potential sorbents are dependent on the process. Should a different process be used, e.g., heating of the aqueous sorbent to drive off NO_x as the regeneration step, a different list of potential sorbents might result.

There were several assumptions on which the screening process was based. It was assumed that except for the sorption step, all the other process steps were reversible and could be carried out at equilibrium. However, there are some steps which are known to be irreversible. Therefore, it was necessary to account for the free energy loss resulting from hydration of the sorbent or reaction with CO_2 to form carbonates.

7.2 Thermodynamic Basis for Screening

Screening of candidate metal oxides can be carried out by considering the free energy changes for the reactions involved in the processes of interest. The overall change in free energy provides the driving force for a process. The object of screening is to select the metal oxide for which the reactions have the most efficient free energy change. It must be large enough to supply driving force for the process, but not too large. If the free energy change in one step of the process is too large, then it is likely that an expensive energy input will be required at some other stage in the process. An example of this is the regeneration step where the free energy change has to be reversed.

The free energy change that we wish to evaluate is the difference between the free energies of two states. The first state of interest is $NO+NO_2$ in the effluent flue gas in which the concentration of $NO+NO_2$ has been reduced to some acceptable level, say 50 ppm. The second state of interest is $NO+NO_2$ gas with the concentration of $NO+NO_2$ equal to the equilibrium partial pressure of $NO+NO_2$ over the scrubber liquid or the dry sorption medium. The free energy of either state is given in equation (7-1).

$$\Delta G = -RT\ln P_{NO_x} \qquad (7\text{-}1)$$

It is convenient to express P_{NO_x} in terms of one component of the mixture of gaseous nitrogen compounds. This is acceptable since all of the components are at equilibrium. We choose either N_2O_3 for nitrite based processes or N_2O_5 for nitrate based processes. The free energy difference between the two states of interest is then given in equation (7-2) for processes based on nitrate formation.

$$\Delta G_{State\ 1} - \Delta G_{State\ 2} = \left[-RT\ell nP_{N_2O_5(State\ 1)}\right] - \left[-RT\ell nP_{N_2O_5(State\ 2)}\right]$$

$$= -RT\ell n\left[\frac{P_{N_2O_5(State\ 1)}}{P_{N_2O_5(State\ 2)}}\right] \qquad (7\text{-}2)$$

In equation (7-2), $P_{N_2O_5(State\ 1)}$ is the partial pressure of N_2O_5 desired in the exit flue gas, i.e., $P_{N_2O_5}$ when P_{NO+NO_2} = 50 ppm. $P_{N_2O_5(State\ 2)}$ is the equilibrium pressure of N_2O_5 over the dry or aqueous sorbent.

According to equation (7-2) the task of thermodynamic screening is as follows: for each metal oxide calculate the partial pressure of N_2O_5 or N_2O_3 over its aqueous solution or over the dry sorbent, $P_{N_2O_5}$ in State 2, and compare that pressure with the pressure of N_2O_5 or N_2O_3 desired in the exit flue gas, $P_{N_2O_5}$ in State 1. Obviously the pressure of N_2O_3 or N_2O_5 must be lower over the sorbent than that desired in the exit flue gas for sorption to occur. In addition, it must be low enough that the term $-RT\ell n(P_{State\ 1}/P_{State\ 2})$ supplies a free energy difference sufficient to provide driving force for the process.

Now let us consider how to calculate the partial pressures of N_2O_3 or N_2O_5 at equilibrium over the metal oxide sorbent. Since both processes start with a dry metal oxide and end with a solid metal nitrite or nitrate, equations (7-3) and (7-4) are valid ones for describing both overall processes.

$$Me(NO_3)_{2(s)} \rightleftarrows N_2O_{5(g)} + MeO_{(s)} \qquad (7\text{-}3)$$

$$Me(NO_2)_{2(s)} \rightleftarrows N_2O_{3(g)} + MeO_{(s)} \qquad (7\text{-}4)$$

It was assumed that all the steps in the process approach equilibrium and there are no steps other than the sorption step which have excessively large free energy changes. If all other steps could be carried out reversibly then Equations (7-3) and (7-4) can be used for sorption free energy calculations. However, we know there are some steps which cannot be conveniently carried out in a reversible manner. We must therefore account for free energy loss that will occur, for example, due to carbonate formation in either process. This can be done by considering the reverse of reactions (7-5) and (7-6).

$$Me(NO_3)_{2(s)} + CO_{2(g)} \rightleftarrows N_2O_{5(g)} + MeCO_{3(s)} \qquad (7\text{-}5)$$

$$Me(NO_2)_{2(s)} + CO_{2(g)} \rightleftarrows N_2O_{3(g)} + MeCO_{3(s)} \qquad (7\text{-}6)$$

The equilibrium constant for reaction (7-3) is shown in Equation (7-7) where a is the activity.

$$K_{eq}(T) = \frac{a_{N_2O_5(g)}\, a_{MeO(s)}}{a_{Me(NO_3)_{2(s)}}} \qquad (7\text{-}7)$$

If it is assumed that the activities of the solid species are one (which is a good assumption since there are usually no solid solutions formed) then the equilibrium constant is numerically equal to the activity of the gaseous product. The total pressures in which we are interested are low and the temperatures are high. We can therefore assume the fugacity coefficient for the gaseous species are one. Under these conditions the equilibrium constant is numerically equal to the partial pressure of the gaseous product in atmospheres.

The equilibrium constant for a reaction at the temperature of interest can be calculated from standard state thermodynamic properties and heat capacities as a function of temperature. Since the equilibrium constant is numercially equal to $P_{N_2O_5}$ or $P_{N_2O_3}$ in atmospheres, calculation of K_{eq} at the sorption temperature yields the data for $P_{N_2O_5}$ or $P_{N_2O_3}$(State 2) needed for screening.

For reactions (7-5) and (7-6) the same procedure was used. The equilibrium constant is shown in Equation (7-8) where activities of the solid species have been assumed equal to one.

$$K_{eq}(T) = \frac{a_{N_2O_5}(g)}{a_{CO_2}(g)} \qquad (7\text{-}8)$$

The partial pressure of CO_2 in the flue gas was taken to be 0.147 atm, i.e., 14.7%. The standard state for CO_2 used in these calculations was 0.147 atm so that the equilibrium constant is again numercially equal to $P_{N_2O_3}$ or $P_{N_2O_5}$ in atmospheres.

7.3 Data Collection and Calculations

7.3.1 Calculation of N_2O_3 and N_2O_5 Pressures Over the Sorbent

The basic data needed for calculating $P_{N_2O_3}$ or $P_{N_2O_5}$ over the sorbent for both the dry process and the process illustrated in Figure 7-1 are standard state thermodynamic properties and heat capacities as a function of temperature. The data were needed for products and reactants in nitrate and nitrite decomposition reactions (7-3), (7-4), (7-5), and (7-6). Section 8.0 describes the collection and tabulation of the

thermodynamic properties. No thermodynamic data had been published for some of the products and reactants of interest, so the properties were estimated. The estimation methods and the results are also described in Section 8.0.

Using the thermodynamic properties and heat capacities of reactants and products, the equilibrium constants for reactions (7-3), (7-4), (7-5), and (7-6) were calculated as a function of temperature using a previously developed computer program, AIRPOL (PA-016). AIRPOL generates graphs of $\log_{10}K$ as a function of temperature for reactions involving products and reactants for which thermodynamic data have been stored. The computer program normalizes the equilibrium equation to one mole of the first product formed. It is for this reason that the reactions have been written as decompositions with the nitrogen oxides as the first product. The calculated equilibria are numerically equal to the nitrogen oxide partial pressure.

7.3.2 Calculation of N_2O_3 and N_2O_5 Pressures in the Flue Gas

The method for calculating $P_{N_2O_3}$ and $P_{N_2O_5}$ at equilibrium in the flue gas when 50 ppm $NO+NO_2$ are present has been previously described (see T.N. 200-007-03a). Radian's gas phase equilibrium model was used to perform the calculations. Two compositions were used for input to the program: 40 ppm NO + 10 ppm NO_2 and 25 ppm NO + 25 ppm NO_2. The calculated amounts of N_2O_3 present were approximately the same for the two compositions, but the amount of N_2O_5 present differed for different compositions.

7.3.3 Results of Calculations

The results of the calculations of $\log_{10}K$ for reactions (7-3) and (7-4) are given in Figures 7-2 and 7-3 respectively.

FIGURE 7-2

Comparison of N_2O_3 Partial Pressure in Flue Gas and Vapor Pressure of N_2O_3 over Metal Oxide Sorbents

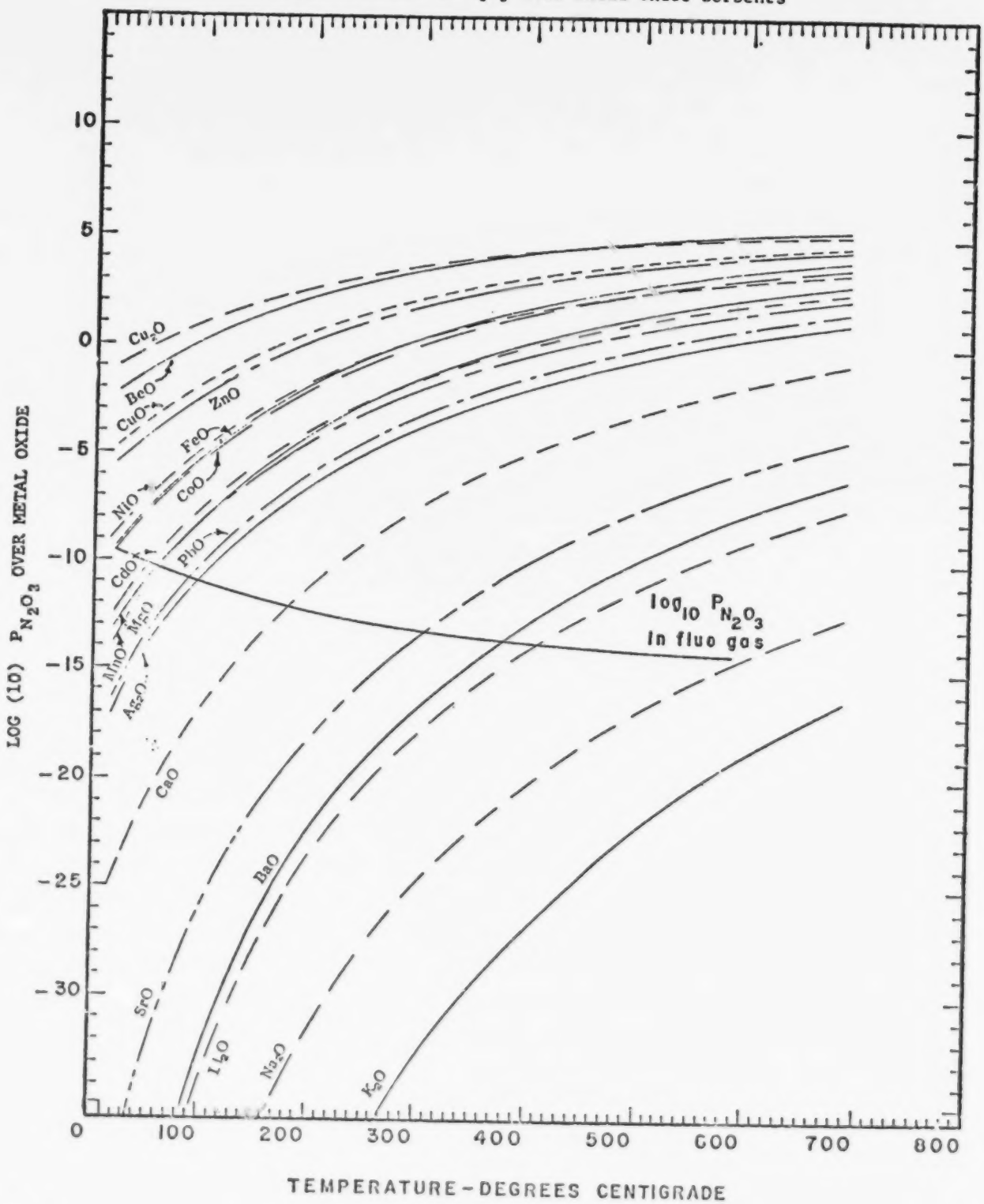
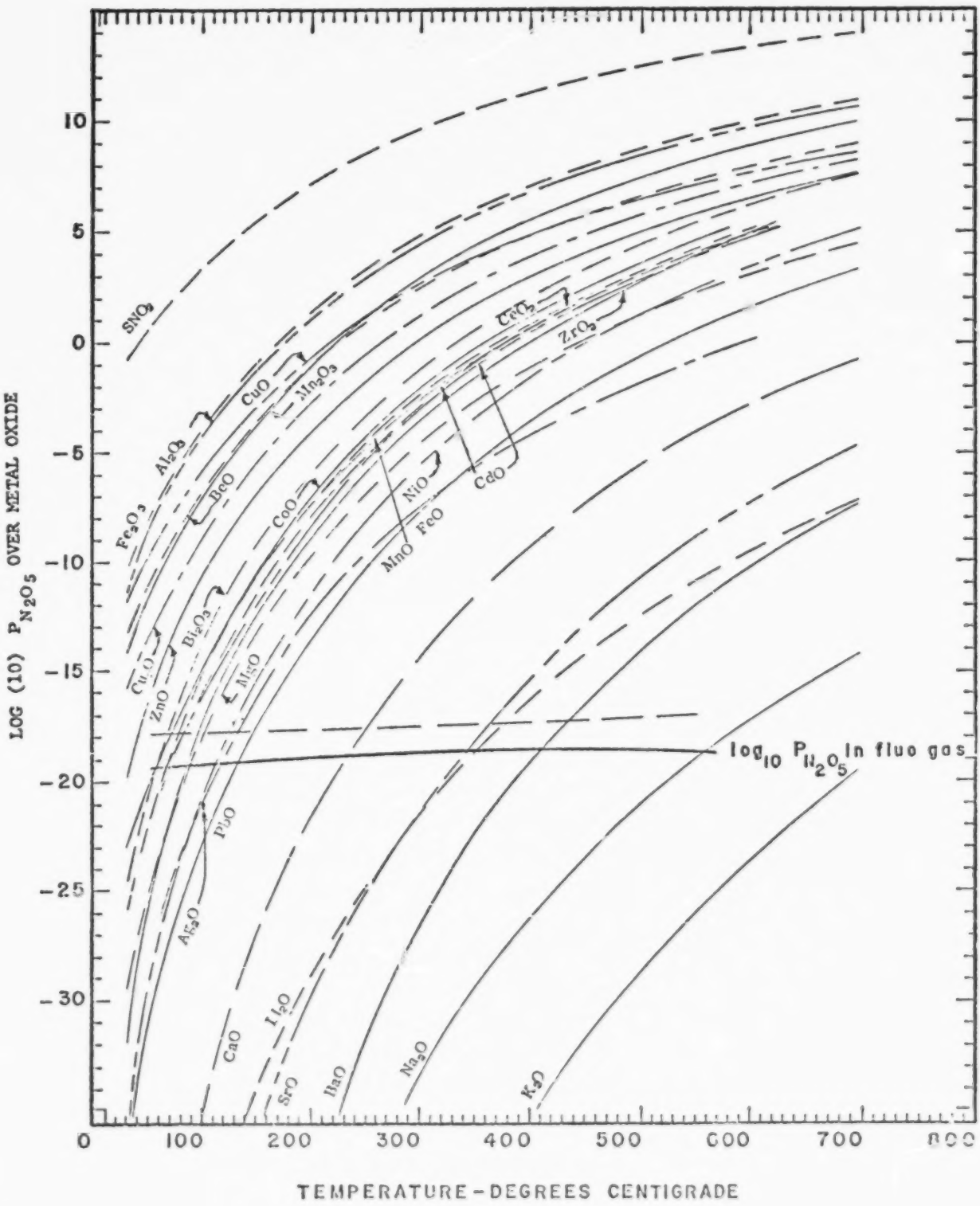


FIGURE 7-3

Comparison of N_2O_5 Partial Pressure in Flue Gas and Vapor Pressure of N_2O_5 over Metal Oxide Sorbents



The data were calculated by the computer program AIRPOL (PA-016), and they show $\log_{10}K_{eq}$ for reactions (7-3) and (7-4) per mole of N_2O_3 or N_2O_5 produced as a function of temperature. The common logarithm of the partial pressure of N_2O_3 or N_2O_5 in the flue gas at 50 ppm NO_x is also plotted on the graphs as a function of temperature. Since the partial pressure of N_2O_3 did not vary greatly for the two compositions considered, only one line was plotted for N_2O_3. However, a broken line and a solid line were plotted for N_2O_5. The broken line indicates $\log_{10}P_{N_2O_5}$ when the flue gas composition is 25 ppm NO and 25 ppm NO_2. The solid line indicates $P_{N_2O_5}$ when the flue gas composition is 40 ppm NO and 10 ppm NO_2.

The results of the calculations of $\log_{10}K$ for reactions (7-5) and (7-6) are shown in Figures 7-4 and 7-5. The logarithms of the partial pressures of N_2O_3 and N_2O_5 in flue gas at 50 ppm NO_x are also plotted on the figures.

7.4 Results of Thermodynamic Screening

7.4.1 General Considerations

The object of the screening process was to select metal oxide sorbents over which the equilibrium vapor pressures of N_2O_3 or N_2O_5 were lower than the desired effluent flue gas pressures of N_2O_3 or N_2O_5. The equilibrium vapor pressures over the sorbent must be low enough compared to flue gas pressures so that the resulting free energy difference is great enough to supply driving force for the process. On the other hand, the vapor pressures cannot be so much smaller that too great a free energy difference results. The reason for this is that the

FIGURE 7-4

Comparison of N_2O_3 Partial Pressure in Flue Gas and Vapor Pressure of N_2O_3 over Metal Carbonate Sorbents

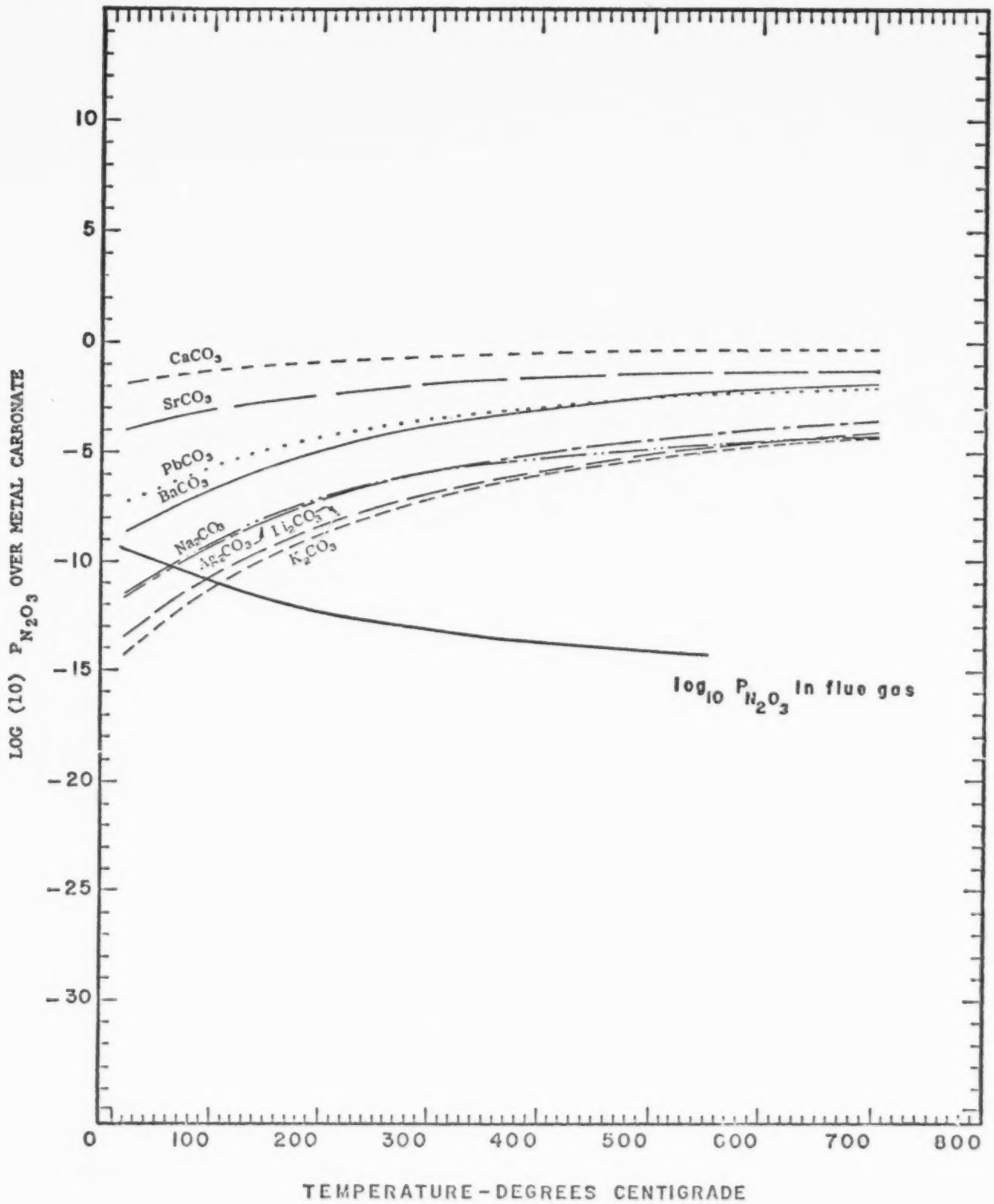
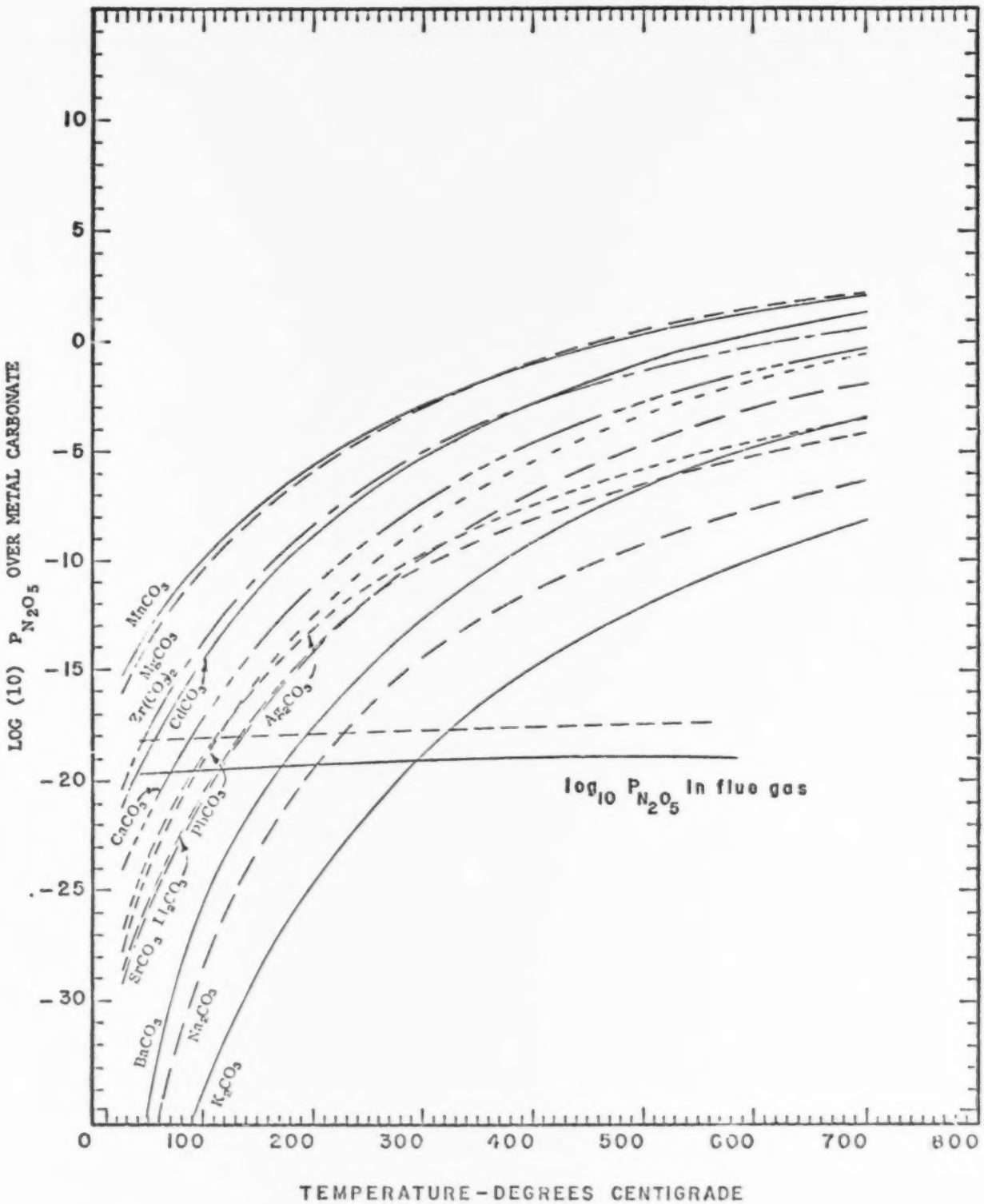


FIGURE 7-5

Comparison of N_2O_5 Partial Pressure in Flue Gas and
Vapor Pressure of N_2O_5 over Metal Carbonate Sorbents



free energy change will have to be reversed in the regeneration step. An expensive energy input will be required to reverse a large free energy change.

The vapor pressures over metal oxides sorbents can be compared to flue gas pressures using Figures 7-2 and 7-3. For the aqueous process screening the pressures were compared at a scrubber temperature of 50°C. For the dry process screening the pressures were compared in the temperature range of 100 to 750°C. To describe processes resulting in nitrite formation the pressures of N_2O_3 over the sorbent were compared with the N_2O_3 pressure in the flue gas. To describe processes resulting in nitrate formation, the pressures of N_2O_5 over the sorbent were compared with the N_2O_5 pressure in the flue gas.

7.4.2 Screening for Dry and Aqueous Processes Based on Nitrite Formation

First let us consider the results of screening for processes which result in nitrite formation. Screening for the aqueous process can be accomplished by comparing $\log_{10} P_{N_2O_3}$ in the flue gas at 50°C with the vapor pressure of N_2O_3 over the metal oxide sorbent at 50°C. If the vapor pressure over the sorbent is greater than, equal to, or only slightly less than the flue gas pressure at 50°C, then the sorbent would not be suitable for an aqueous removal process involving nitrite formation. If the vapor pressure over the sorbent is at least two orders of magnitude less than the flue gas pressure, then sufficient driving force to run the process may result. The metal oxide would be suitable for further consideration as a sorbent. Based on the reasoning described above and the data in Figure 7-2, the oxides BeO, CdO, CoO, Cu_2O, CuO, FeO, MgO,

MnO, NiO, and ZnO were judged unsuitable for use in an aqueous sorption process involving nitrite formation. The nitrites of these metal oxides are too unstable to sorb $NO+NO_2$ at 50°C. In fact, no evidence for the existence of nitrites of BeO, Cu_2O, FeO, MnO, or ZnO has been reported in the literature. It was not possible to calculate N_2O_3 pressures over the nitrites of Al_2O_3, Bi_2O_3, CeO_2, Fe_2O_3, Mn_2O_3, SnO_2 or ZrO_2 because of our inability to estimate some of the thermodynamic properties needed. However, again we found no evidence in the literature for the existence of these nitrites.

Screening for the dry process resulting in nitrite formation can also be accomplished using the data in Figure 7-2. For the dry process comparison of N_2O_3 vapor pressures over the sorbent with flue gas pressures was made at temperatures above 100°C. The same reasoning was used for the dry process screening as was used for the aqueous process. It was found that all of the metal oxides that were unsuitable for the aqueous process at 50°C were also unsuitable for the dry process at 100°C for the same reason: vapor pressure of N_2O_3 over the sorbent was greater than or equal to $P_{N_2O_3}$ in the flue gas. In addition, the above was also true for PbO and Ag_2O at 100°C, although these oxides were suitable for the aqueous nitrite process at 50°C. The same results for Al_2O_3, Bi_2O_3, CeO_2, Fe_2O_3, Mn_2O_3, SnO_2, and ZrO_2 hold for the dry process as well as the aqueous.

In summary, it appears that the oxides Ag_2O, BaO, CaO, K_2O, Li_2O, Na_2O, PbO, and SrO remain to be considered as sorbents for an aqueous process at 50°C involving nitrite formation. For a dry process at 100°C involving nitrite formation, the same candidate oxides except for PbO and Ag_2O remain. These results are summarized in Table 7-2.

TABLE 7-2

METAL OXIDES UNSUITABLE FOR USE IN PROCESSES BASED ON NITRITE FORMATION

Dry Process	Aqueous Process
Ag_2O	BeO[1]
BeO[1]	CdO
CdO	CoO
CoO	Cu_2O[1]
Cu_2O[1]	CuO
CuO	FeO[1]
FeO[1]	MgO
MgO	MnO[1]
MnO[1]	NiO
NiO	ZnO[1]
PbO	Al_2O_3[1,2]
ZnO[1]	Bi_2O_3[1,2]
Al_2O_3[1,2]	CeO_2[1,2]
Bi_2O_3[1,2]	Fe_2O_3[1,2]
CeO_2[1,2]	Mn_2O_3[1,2]
Fe_2O_3[1,2]	SnO_2[1,2]
Mn_2O_3[1,2]	ZrO_2[1,2]
SnO_2[1,2]	
ZrO_2[1,2]	

1. No evidence for existence of the nitrite was found in the literature.
2. Thermodynamic properties for the nitrite could not be estimated. Therefore, no partial pressure calculations could be made to predict nitrite stability.

7.4.3 Screening for Dry and Aqueous Processes Based on Nitrate Formation

Screening the sorbents for use in processes based on nitrate formation was accomplished by comparing vapor pressures of N_2O_5 over the sorbent with flue gas N_2O_5 pressure at 50°C for the aqueous process and 100°C for the dry process. Using the data in Figure 7-3 it was found that the vapor pressure of N_2O_5 over the sorbent at 50°C was greater than or approximately equal to that in the flue gas for the oxides Al_2O_3, BeO, Bi_2O_3, CoO, Cu_2O, CuO, FeO, Fe_2O_3, Mn_2O_3, NiO, SnO_2, and ZnO. These oxides were therefore eliminated from consideration as sorbents in aqueous nitrate forming processes. At 100°C those oxides mentioned above plus the oxides CdO, CeO_2, MgO, and ZrO_2 were found to give vapor pressures of N_2O_5 greater than or approximately equal to the N_2O_5 pressure in the flue gas. These oxides were therefore no longer considered as candidate sorbents for dry nitrate-forming processes.

In summary it was found that the oxides Ag_2O, BaO, CaO, Cs_2O, K_2O, Li_2O, Na_2O PbO, and SrO would be suitable for use in both the dry and the aqueous process based on nitrate formation. In addition, the oxides CdO, CeO_2, MgO, MnO, and ZrO_2 remain as possible sorbent candidates for the aqueous nitrate-forming process only. These results are summarized in Table 7-3.

7.4.4 Screening Metal Carbonate Sorbents

Some of the steps in the processes under consideration will probably be irreversible and will involve dissipation of free energy that would otherwise be available for driving force

TABLE 7-3

METAL OXIDES UNSUITABLE FOR USE IN PROCESSES BASED ON NITRATE FORMATION

Dry Process	Aqueous Process
Al_2O_3	Al_2O_3
BeO	BeO
Bi_2O_3	Bi_2O_3
CdO	CoO
CeO_2	Cu_2O[1]
CoO	CuO
Cu_2O[1]	FeO
CuO	Fe_2O_3
FeO	Mn_2O_3[1]
Fe_2O_3	NiO
MgO	SnO_2
MnO	ZnO
Mn_2O_3[1]	
NiO	
SnO_2	
ZnO	
ZrO_2	

1. No evidence was found in the literature for existence of the nitrate.

for the process. One step that is anticipated to so reduce the available free energy is that of carbonate formation by sorption of CO_2 present in the flue gas. The reduction in available free energy due to carbonate formation can be taken into account by considering reactions (7-5) and (7-6). Vapor pressures of N_2O_3 and N_2O_5 over metal carbonate sorbents in the presence of 14.7% CO_2 were obtained by calculating log K for reactions (7-5) and (7-6). Those pressures calculated in the presence of CO_2 were again compared to flue gas pressures to complete the screening process. Calculations were done only for those metal carbonates whose oxides were not eliminated on the basis of nitrite or nitrate instability.

The data in Figure 7-4 were used for screening carbonate sorbents for dry and aqueous processes involving nitrite formation. Again, the vapor pressure of N_2O_3 over the sorbent must be at least two orders of magnitude less than the pressure of N_2O_3 in the flue gas. For the aqueous nitrite forming process at 50°C, potassium is the only suitable sorbent. Lithium is a borderline case. For the dry nitrite forming process at 100°C, no metal carbonate sorbent is suitable.

To screen metal carbonate sorbents for nitrate forming processes, the data shown in Figure 7-5 were used. It was found that for aqueous nitrate forming processes, all of the sorbents considered were suitable except for CdO, MgO, MnO, and ZrO_2. It was found that for dry nitrate forming processes, none of the sorbents were suitable except for BaO, K_2O, Na_2O, and SrO (borderline).

7.4.5 Summary and Conclusions

Metal oxide sorbents were screened for applicability in dry or aqueous, regenerative NO_x sorption processes. The screening was done on the basis of the thermodynamics of the reactions between the metal oxides and nitrogen oxides. The free energy difference between two states of interest was investigated. One state was the equilibrium vapor pressure of the nitrogen oxide species over the dry or aqueous sorbent. The other state of interest was the equilibrium concentration of the nitrogen oxide species in the flue gas at 50 ppm $NO+NO_2$.

A sorbent was sought such that the free energy difference between the two states of interest was great enough to provide driving force for the removal process. For some sorbents, the vapor pressure of the gaseous nitrogen compound over the sorbent was greater than the equilibrium partial pressure desired in the flue gas. Those sorbents which were judged unsuitable on the basis of nitrite instability were BeO, CdO, CoO, Cu_2O, CuO, FeO, MgO, MnO, NiO, ZnO, Al_2O_3, Bi_2O_3, CeO_2, Fe_2O_3, Mn_2O_3, SnO_2, and ZrO_2. Those which were judged unsuitable on the basis of nitrate instability were Al_2O_3, BeO, Bi_2O_3, CoO, Cu_2O, CuO, FeO, Fe_2O_3, Mn_2O_3, NiO, SnO_2 and ZnO.

Further calculations were made taking into account that the presence of CO_2 in the flue gas would reduce the free energy difference available for driving force. The result of those calculations was that potassium is the only oxide suitable for use in a nitrite forming process. For nitrate forming processes Ag_2O, BaO, CaO, K_2O, Li_2O, Na_2O, PbO, and SrO are potential sorbents. The results are summarized in Table 7-4.

TABLE 7-4

POTENTIAL SORBENTS AFTER SCREENING

Nitrite Forming Processes		Nitrate Forming Processes	
Aqueous Process	Dry Process	Aqueous Process	Dry Process
K_2O	None	Ag_2O	BaO
(Li_2O)		BaO	K_2O
		CaO	Na_2O
		K_2O	SrO
		Li_2O	
		Na_2O	
		PbO	
		SrO	

It should be re-emphasized that the screening described here is based upon the formation of a solid nitrate or nitrite. Processes in which solids are not formed, e.g., heating of the liquid to drive off sorbed NO_x, could be based upon some of the metal cations screened out in this study.

8.0 THERMODYNAMIC PROPERTIES

One of the most important requirements for creating a theoretical description of aqueous NO_x scrubbing are thermodynamic properties of nitrogen oxides, oxyacids and their sorption products. The thermodynamic data of interest include standard state properties of formation and heat capacities of compounds and temperature dependence of equilibrium constants for dissociation, dissolution, decomposition, and vaporization reactions. Data such as these were used in the gas phase and aqueous phase equilibrium models and in thermodynamic screening. They are also needed in engineering evaluation of experimental sorption data.

The data must be collected mainly from the literature. To measure even one equilibrium constant or heat of formation would require several months of work. After data were located in the literature they had to be considered carefully and usually converted to a form consistent with other data being used. Often, differing values for the same constant are reported. Then, a decision must be made concerning which value to use. If a value for a particular constant of interest is not reported in the literature, it must be calculated or estimated. The following sections describe the collection of thermodynamic properties of interest, the evaluation of data, and how the data were used in the theoretical description.

8.1 Standard State Thermodynamic Properties and Heat Capacity Data

If the standard state heat of formation, absolute entropy, and heat capacity as a function of temperature of products and reactants are known, the change in free energy

and thus the equilibrium constant as a function of temperature for a reaction can be calculated directly. Therefore, values of these thermodynamic properties were compiled for the gaseous nitrogen oxides and oxyacids, and solid metal nitrates, nitrites, and hydroxides. Data for single and double metal oxides, metal carbonates, sulfites, sulfates, and sulfides and elements had been collected, evaluated, and compiled as described previously (PA-016). The sources of data were compilations of thermodynamic properties (ST-006, ST-017, ST-018, ST-019, RO-007, WA-001, WA-018, LA-008, KE-009 - KE-014, CO-048 and KU-003) as well as the open literature which was surveyed using Chemical Abstracts. Published data were available for all the gaseous compounds of interest. However, some of the data for solid metal nitrates and nitrites could not be found in the literature. Those data were estimated using estimation methods developed previously (PA-016). The standard state properties and heat capacities were stored in a computer data base. A storage and retrieval program was used including options by which the free energy change and equilibrium constant for a reaction can be calculated from the stored thermodynamic properties. The details of the standard state thermodynamic property compilation are given in T.N. 200-007-04a which is included in Volume II of this report. The note includes a copy of the entire data base including the bibliography as well as a description of the selection of a value when differing values were reported.

The standard state properties and heat capacities stored in the data base were used as follows:

> to calculate equilibrium constants as a function of temperature for reactions considered in the gas phase equilibrium model (Section 4.0),

to calculate equilibrium constants as a function of temperature for chemical reactions involved in the thermodynamic screening process (Section 7.0).

The computer program used for data storage and retrieval also calculates and plots equilibrium constants versus temperature. The calculations and the plots generated for this work are contained in Technical Note 200-007-15 in Volume II of this report.

8.2 Measured Equilibrium Constants

Equilibrium constants for some of the reactions of interest for the theoretical description had been measured and reported in the literature. The reactions of interest for which constants were reported and evaluated are shown in equations 8-1 through 8-5.

$$HNO_{3(g)} \rightleftarrows HNO_{3(\ell)} \quad (8\text{-}1)$$

$$HNO_{3(\ell)} \rightleftarrows H^+ + NO_3^- \quad (8\text{-}2)$$

$$HNO_{2(g)} \rightleftarrows HNO_{2(\ell)} \quad (8\text{-}3)$$

$$HNO_{2(\ell)} \rightleftarrows H^+ + NO_2^- \quad (8\text{-}4)$$

$$NO_{(g)} \rightleftarrows NO_{(\ell)} \quad (8\text{-}5)$$

For the reactions involving liquid phase species, both equilibrium constants and activity coefficients were needed. The literature was searched from 1960 using Chemical Abstracts

to obtain equilibrium constant and activity coefficient data. A compilation (SI-001) covered the open literature up to 1960. The original articles were studied; some had to be translated. In some cases the data had to be recalculated because activity coefficients were not used to calculate the equilibrium constant or the units were not on a consistent basis with other units used by Radian. A detailed description of the references and data considered for each constant is given in Technical Note 200-007-11, entitled "Selected Values for Equilibrium Constants Used in the Aqueous Equilibrium Formulation". The note is included in Volume II of this report. The selected and recalculated constants are shown in Table 8-1.

TABLE 8-1

Selected Values for Equilibrium Constants

Reaction	Form of Constant	Selected Values	Reference
$HNO_{3(\ell)} \rightleftarrows H^+ + NO_3^-$	$K = \frac{a_{H^+} a_{NO_3^-}}{a_{HNO_{3(\ell)}}}$	$K_{25°C} = 26.9$ $\log K = 6.557 - \frac{320.88}{T} - .01359T$	HE-001
$HNO_{3(g)} \rightleftarrows HNO_{3(\ell)}$	$K = \frac{a_{HNO_{3(\ell)}}}{P_{HNO_{3(g)}}}$	$K_{25°C} = 5.80 \times 10^{4}$ atm^{-1}	DA-012
$HNO_{2(\ell)} \rightleftarrows H^+ + NO_2^-$	$K = \frac{a_{H^+} a_{NO_2^-}}{a_{HNO_{2(\ell)}}}$	$K_{25°C} = 7.24 \times 10^{-4}$ $\log K = 34.558 - \frac{5.8554 \times 10^{3}}{T} - 60.571 \times 10^{-3}T$	LU-005 TU-007
$HNO_{2(g)} \rightleftarrows HNO_{2(\ell)}$	$K = \frac{a_{HNO_{2(\ell)}}}{P_{HNO_{2(g)}}}$	$K_{25°C} = 2.155 \times 10$ atm^{-1}	AB-006
$NO_{(g)} \rightleftarrows NO_{(\ell)}$	$K = \frac{a_{NO_{(\ell)}}}{P_{NO_{(g)}}}$	$K_{20°C} = 2.10 \times 10^{-3}$ atm^{-1}	WI-029

9.0 SUMMARY OF RESULTS

This study was undertaken to develop a theoretical description of alkaline scrubbing processes for removing NO and NO_2 from electric utility plant flue gases. The first task was to define the problem using what had already been published in the literature. The problem was defined for the SO_2-free system. It was found that the nitrogen oxides - water system is very complicated due to the many stable oxidation states of nitrogen and the variety of gaseous and aqueous molecules and ions that exist in equilibrium. It was further found that the application of aqueous scrubbing to treatment of gases having the composition of power plant flue gases had not been studied previously.

The molar composition of a gas mixture containing NO, NO_2, and H_2O affects the concentration of each individual nitrogen-oxygen species quite markedly due to the large number of possible equilibrium reactions. Therefore a composition-concentration model was developed which calculates the gas phase concentrations of each of the species present at equilibrium under specified conditions of temperature, total pressure, and chemical composition (total moles of NO, NO_2, and H_2O). Calculations done using this model were used to explain why N_2O_4 is the molecule involved in the mass transfer mechanism and in the rate limiting step for processes such as nitric acid manufacture where NO_2 is present in larger quantities than NO. The calculations showed further that the same mechanism and rate limiting step proposed for a particular sorption process such as nitric acid manufacture or sorption from nitric acid plant tail gases cannot be applied to aqueous processes for treating flue gas.

A new mechanism was proposed for this previously undefined problem. From calculations done using the equilibrium concentration model it was proposed that vapor film limited diffusion of HNO_2 and HNO_3 is the mechanism for NO_x sorption from flue gases. Liquid film limited sorption of NO_2 may also be important in the mechanism.

A limited amount of sorption data were analyzed according to this mechanism. The data were collected in connection with an EPA in-house experimental program for studying alkaline sorption of NO_x. Data analysis using the proposed mechanism gave results which agreed with experimental findings.

Thermodynamic properties of gaseous nitrogen-oxygen compounds, aqueous sorption products and solid metal nitrates and nitrites were compiled and unpublished values for the solids were estimated. The thermodynamic data were used to screen metal oxide sorbents for wet or dry NO_x removal processes based on formation of a solid metal nitrate or nitrite and regeneration of the metal oxide sorbent. The results of the thermodynamic screening apply to any regenerative process involving formation of solid metal nitrates or nitrites.

10.0 BIBLIOGRAPHY

AN-001 Andrew, S. P. S. and D. Hanson, "The Dynamics of Nitrous Gas Absorption", Chem. Eng. Sci. 14, 105-13 (1961).

AS-004 Ashmore, P. G. and B.J. Tyler, "The Formation and Thermodynamic Properties of Nitrous Acid Vapour", J. Chem. Soc.. London 1961, 1017-21 (1961).

AT-005 Atroshchenko, V. I., "Absorption of Nitrogen Oxides by Alkaline Solutions and the Influence of the State of the Gas and Liquid Phases", Ukrain. Khem. Zhur. 12 442-59 (1937).

BA-003 Bartok, W., et al., Systems Study of Nitrogen Oxide Control Methods for Stationary Sources, prepared for NAPCA under Contract No. PH 22-68-55, Esso Research and Engineering Co., 1969.

BE-023 Beattie, I. R. and S. W. Bell, "Dinitrogen Trioxide. Part I. Stability in the Gaseous Phase", J. Chem. Soc., London 1957, 1681-6 (1957).

BR-002 Brown, G. G., et al., Unit Operations, John Wiley and Sons, New York, 1950.

BU-009 Bunton, C. A. and G. Stedman, "Absorption Spectra of Nitrous Acid in Aqueous Perchloric Acid", J. Chem. Soc., London 1958, 2440-4 (1958).

CA-014 Caudle, P. G. and K. G. Denbigh, "Kinetics of the Absorption of Nitrogen Peroxide into Water and Aqueous Solutions", Trans. Far. Soc. 49, 39-52 (1953).

CA-069 Carrington, Tucker and Norman Davidson, "Photoelectric Observation of the Rate of Dissociation of Nitrogen Tetroxide by a Shock Wave", J. Chem. Phys. 19, 1313 (1951).

CH-032 Chilton, T. H., "The Chemistry of Nitrogen Oxides", Strong Water, Chapter 2, pp. 25-59, MIT Press, Cambridge, Mass., (1968).

CO-048 Coughlin, James P., Contributions to the Data on Theoretical Metallurgy. Part XII: Heats and Free Energies of Formation of Inorganic Oxides, U.S. Bureau of Mines Bulletin 542, (1954).

EL-004 Elenkov, D. and Iv. Krustev, "Kinetics and Mechanism of the Absorption of Nitrogen Oxides in Alkaline Solutions", Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk 2(4), 771-80 (1969).

GA-008 Ganz, S. N., et al., "Absorption of Nitrogen Oxides with Milk of Lime in Mechanical Absorbers", Izv. Vysshikh Uchebn. Zavedeniĭ, Khim. i Khim. Tekhnol. 5(1), 155-9 (1962).

GA-009 Ganz, S. N., "Kinetics of Nitric Acid Formation in Rapidly Revolving Mechanical Absorbers", Zhur. Prikl. Khim. 28, 1037-48 (1955).

GA-010 Ganz, S. N. and S. B. Kravchinskaya, "Rate of Absorption of Nitrogen Oxides by Ca(OH)$_2$ Solutions in Mechanical Absorbers with Higher R.P.M.", J. Appl. Chem. (USSR) 28, 133-41 (1955).

GA-013 Ganz, S. N., "Effect of Hydrodynamic Condition on the Rate of Absorption of Nitrogen Oxides by Solutions of Calcium Hydroxide in a Mechanical Absorber on a Semi-plant Scale. I.", J. Appl. Chem. (USSR) 30, 1383-91 (1957).

GA-014 Ganz, S. N. and M. A. Lokshin, "Influence of Fundamental Physicochemical Factors on the Absorption Rate of Nitrogen Oxides in $Ca(OH)_2$ Solution in High-Speed Mechanical Absorbers", Zh. Prikl. Khim. 30(10), 1525-35 (1957); J. Appl. Chem. USSR 30, 1592-1600 (1957).

GA-046 Garcia, L. H., "Absorption Studies of Equimolar Concentrations of NO and NO_2 in Alkaline Solutions", Presented at the Second International Lime/Limestone Wet Scrubbing Symposium, New Orleans, Louisiana, November 8-12, 1971.

GO-007 Gorfunkel, V. E. and Ya. I. Kil'man, "Preparation of Solutions of Calcium Nitrite-Nitrate by Absorption of Nitrogen Oxides from Nitrose Gas Tailing with Milk of Lime. II.", Rererat. Zhur., Khim. 1958, Abstr. No. 1875, Chem. Abstracts 53: 12599g.

GR-004 Gray, P. and A. D. Yoffee, "The Reactivity and Structure of Nitrogen Dioxide", Chem. Rev. 55, 1069-1154 (1955).

HO-009 Hofmeister, H. K. and R. Kohlhaas, "Absorption of NO-NO_2 Mixtures by a Laminar Water Jet", Ber. Bunsenges. Physik. Chem. 69(3), 232-8 (1965).

KE-009 Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. Part XIII: High-Temperature Heat Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds, U.S. Bureau of Mines Bulletin 584, (1960).

KE-010 Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. Part X: High-Temperature Heat-Content, Heat Capacity, and Entropy Data for Inorganic Compounds, U.S. Bureau of Mines Bulletin 476, (1949).

KE-011 Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy. Part VIII: The Thermodynamic Properties of Metal Carbides and Nitrides, U.S. Bureau of Mines Bulletin 407, (1937).

KE-012 Kelley, K. K. and E. G. King, Contributions to the Data on Theoretical Metallurgy. Part XIV: Entropies of the Elements and Inorganic Compounds, U.S. Bureau of Mines Bulletin 592, (1961).

KE-013 Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. Part V: Heats of Fusion of Inorganic Substances, U.S. Bureau of Mines Bulletin 393, (1936).

KE-014 Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. Part III: The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances, U.S. Bureau of Mines Bulletin 383, (1935).

KO-024 Koval, E. J. and M. S. Peters, "How Does Nitric Oxide Affect Reactions of Aqueous Nitrogen Dioxide?", Ind. Eng. Chem. 52, 1011-14 (1960).

KO-026 Koval, E. J., Influence of Nitric Oxide on Aqueous Nitrogen Dioxide Reactions, Dissertation, Univ. of Illinois (Urbana), (1958).

KR-006 Kramers, H., M. P. P. Blind, and E. Snoeck, "Absorption of Nitrogen Tetroxide by Water Jets", Chem. Eng. Sci. 15, 115-23 (1961).

KR-007 Krustev, Iv., "Absorption of Nitrogen Oxides by Solutions Containing Sodium Carbonate, Sodium Nitrite and Sodium Nitrate", Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk. 1(1), 109-23 (1968).

KR-008 Krustev, Iv., "Absorption of Nitrogen Oxides by Sodium Carbonate Solutions under Industrial Conditions", Khim. Ind. (Sofia) 1968(4), 147-51 (1968).

KU-003 Kubaschewski, O., et al., Metallurgical Thermochemistry, 4th Edition, Pergamon Press, 1967.

LA-008 Landolt-Börnstein, "Kalorische Zustandsgrössen", 2(4), Springer-Verlag, Berlin, 1961.

LO-007 Lowell, P. S., et al., A Theoretical Description of the Limestone Injection Wet Scrubbing Process, Vol. 1, Final report for NAPCA Contract No. CPA-22-69-138, Austin, Texas, Radian Corp., 1970, PB 193-029.

MI-004 Millen, D. J., J. D. S. Goulden, and C. K. Ingold, "The Ion $N_2O_3^+$: Binding by One-Electron Transfer", Nature 165, 565 (1950).

MI-005 Mirev, D., et al., "Absorption of Nitrogen Oxides by Vibrating Layers of NaOH Solutions", Compt. Rend. Acad. Bulgare Sci. 14, 259-62 (1961).

MO-008 Moll, Albert James, The Rate of Hydrolysis of Nitrogen Tetroxide, Dissertation, Univ. of Washington, 1966.

MU-004 Mucskai, L., "Absorption Kinetics of Nitrogen Oxides. II.", Magy. Kem. Folyoirat 72(8), 354-62 (1966).

PA-016 Parsons, Terry, Gary D. Schroeder, and David DeBerry, Applicability of Metal Oxides to the Development of New Processes for Removing SO_2 from Flue Gases, 2 vols., Final Report for NAPCA Contract No. PH 86-68-68, Austin, Texas, Tracor, Inc., 1969, PB 185 562.

PE-010 Perel'man, S. and L. Kantorovich, "The Alkaline Absorption of Nitrogen Oxides", J. Chem. Ind. (USSR) 17(6), 3-9 (1940).

PO-015 Pozin, M. E., et al., "The Absorption of Nitrogen Oxides in Soda Solutions in the Penn Apparatus for the Production of Sodium Nitrate", Trudy Leningrad. Teknol. Inst. im. Lensoveta 36, 120-32 (1956).

RO-007 Rossini, F. D., et al., Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, 1952.

SI-001 Sillén, L. G., Stability Constants of Metal-Ion Complexes, Section I: Inorganic Ligands, Special Publication No. 17, London: The Chemical Society, Burlington House, 1964.

ST-006 Stull, D. R., et al., JANAF Thermochemical Tables, Midland, Michigan, Dow Chemical Co., PB 168 370, 1965.

ST-012 Streight, H. R. L., "Reduction of Oxides of Nitrogen in Vent Gases", Can. J. Chem. Eng. 36, 3-11 (1958).

ST-017 Stull, D. R., et al., JANAF Thermochemical Tables - First Addendum, Midland, Michigan, Dow Chemical Co., PB 168 370-1, August, 1966.

ST-018 Stull, D. R., et al., JANAF Thermochemical Tables - Second Addendum, Midland, Michigan, Dow Chemical Co., PB 168 370-2, August, 1967.

ST-019 Stull, D. R., et al., JANAF Thermochemical Tables - Third Addendum, Midland, Michigan, Dow Chemical Co., PB 168 370-3, August, 1968.

ST-026 Stern, Kurt H., High Temperature Properties and Decomposition of Inorganic Salts, Part 3, Nitrates and Nitrites, Preprint, Available from NSRDS-NBS around May, 1971.

VA-006 Varlamov, M. L. and O. M. Drobysheva, "Absorption of Nitrogen Oxides in Low Concentrations by Sodium Carbonate Solutions in an Apparatus of the Venturi-Tube Type", Izvest. Vysshikh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol. 3(1), 146-50 (1960).

VA-009 Varlamov, M. L. and O. M. Drobysheva, "Mass Transfer and Chemical Reaction in a Venturi Scrubber", Zhur. Priklad. Khim. 33, 2020-9 (1960); J. Appl. Chem. (USSR) 33, 1997-2004 (1960).

VO-007 Vosper, Alan J., "Dissociation of Dinitrogen Tetroxide in the Gas Phase", J. Chem. Soc. A. 1970, 625-27 (1970).

WA-001 Wagman, D. D., et al., "Selected Values of Chemical Thermodynamic Properties. Tables for Elements 35 through 53 in the Standard Order of Arrangement", NBS Technical Note 270-4, Washington, D. C., GPO, May, 1969.

WA-006 Waldorf, D. M. and A. L. Babb, "Absorption Spectrum at 357 mu in the Nitrogen Oxides-Water System", J. Chem. Physics 40(6), 1476-7 (1964).

WA-014 Wayne, L. G. and D. M. Yost, "Kinetics of the Rapid Gas Phase Reaction between NO, NO_2 and H_2O", J. Chem. Physics 19(1), 41-7 (1951).

WA-015 Waldorf, D. M., Reactions and Equilibria in the Nitrogen Oxides-Water System, Dissertation, Univ. of Washington, 1962.

WA-016 Wayne, L. G. and D. M. Yost, "Rate of the Rapid Gas Phase Reaction between NO, NO_2, and H_2O", J. Chem. Physics 18, 767-8 (1950).

WA-018 Wagman, D. D. et al., "Selected Values of Chemical Thermodynamic Properties. Tables for the First Thirty-Four Elements in the Standard Order of Arrangement", NBS Technical Note 270-3, Washington, D. C., GPO, January, 1968.

ZH-001 Zhavoronkov, N. M., et al., "The Study of Absorption of Nitrogen Oxides by Alakaline Solutions in Columns with Filler Bodies", Khim. Prom. 1954, 419-23 (1954).

ZH-002 Zhavoronkov, N. M. and Yu. M. Martynov, "The Kinetics of the Absorption of Nitrogen Oxides by Water and Aqueous Solutions of Nitric Acid", Khim. Prom. 1959, 150-5 (1959).